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OCCURRENCE AND DISTRIBUTION OF POTENTIALLY VOLATILE TRACE ELEMENTS IN COAL

R. R. Ruch, et al

Illinois State Geological Survey

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The report gives results of complete chemical analyses of 101 whole coal samples and of 32 separate fractions of four laboratory prepared (washed) coals. Trace elements determined were: Sb, As, Be, B, Br, Cd, Cr, Co, Cu, F, Ga, Ge, Pb, Mn, Mo, Ni, Hg, P, Se, Sn, V, Zn, and Zr. In addition, the following major and minor elements were determined: Al, Ca, Cl, Fe, Mg, K, Si, Na, S, and Ti. Standard coal analyses--proximate, ultimate, heating value, sulfur varieties, and ash--are also reported. Wherever possible, accuracy was evaluated by comparing results obtained by the various methods with results from splits of the same coal samples. Analytical procedures given in detail include: neutron activation, optical emission, atomic absorption, X-ray fluorescence, and ion-selective electrode. Certain techniques were chosen for determining specific elements because they are more accurate, their precision is superior, or they take less time for analysis. Further comparisons, based on analyzing whole coal and its low- and high-temperature ashes, permitted a thorough evaluation of trace-element losses resulting from volatilization during sample preparation.

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Trace Elements	Analytical Techniques	06F
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OCCURRENCE AND DISTRIBUTION OF POTENTIALLY VOLATILE TRACE ELEMENTS IN COAL:

A Final Report

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ABSTRACT

Chemical analyses of 101 whole coal samples and of 32 separate fractions of four laboratory-prepared (washed) coals have been made in the laboratories of the Illinois State Geological Survey. The four laboratory-prepared coals and eighty-two of the 101 whole coals are from the Illinois Basin. The remaining 19 coal samples were collected from other parts of the United States.

Trace elements determined were antimony (Sb), arsenic (As), beryllium (Be), boron (B), bromine (Br), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), fluorine (F), gallium (Ga), germanium (Ge), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), mercury (Hg), phosphorus (P), selenium (Se), tin (Sn), vanadium (V), zinc (Zn), and zirconium (Zr). Major and minor elements determined were aluminum (Al), calcium (Ca), chlorine (Cl), iron (Fe), magnesium (Mg), potassium (K), silicon (Si), sodium (Na), sulfur (S), and titanium (Ti). Procedures for the analytical methods used—neutron activation, optical emission, atomic absorption, X-ray fluorescence, and ion-selective electrode—are given in detail.

Wherever practical, accuracy was evaluated by comparing results obtained by the various methods from splits of the same coal samples. Further comparisons were made by analyzing whole coal and its low- and high-temperature ashes, thus permitting a thorough evaluation of trace-element losses resulting from volatilization during sample preparation.

In general, results from the various analytical procedures compared favorably, although exceptions are noted, e.g., from V and from F. Certain techniques have been chosen as preferred methods for determining specific elements because they are more accurate, their precision is superior, or they take less time for analysis.

Statistical analyses of the large amounts of data generated on the 101 whole coal samples have resulted in several preliminary findings:

1. The elements Al, Fe, F, Ga, Br, B, Be, Cr, Cu, K, Ni, Si, Ti, Se, and V display a more or less normal distribution of analytical values with small standard deviations and ranges. A second group is composed of Cd, Zn, P, As, Sb, Pb, Sn, Cl, Ge, and Hg, each of which exhibits highly skewed distributions with large ranges and standard deviations.
2. The highest positive correlation coefficient (r) for any two chemical elements in coal is that between Zn and Cd ($r = 0.93$). Other significant positive correlations were found between the elements within the following groups: As, Co, Cu, Ni, Pb, and Sb; Si, Al, Ti, and K; Mn and Ca; and Na and Cl.
3. The average concentration of an element in the earth's crust (the clarke value) was compared to the mean value of that element in coal. Only three elements were found to be enriched in coals by at least one order of magnitude: Cd, B, and Se. Similarly, only three elements, F, Mn, and P, were found to be depleted in the coals by at least one order of magnitude.

The data from the analytical determinations on the washed coals are plotted as washability curves and as histograms. These data allow the elements to be classified into four groups. The elements in the first group (Ge, Be, and B) have the greatest organic affinity and tend to be concentrated in the clean coal fractions. The elements in the second group (Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo) are those found concentrated in the mineral matter in coal and have the least organic affinity. A third group (P, Ga, Ti, Sb, and V) contains elements which are apparently associated both organically and inorganically in coals but are more closely allied to the elements with the highest organic affinities. The last group contains those elements (Co, Ni, Cr, Se, and Cu) which are also found in both modes of combination but which tend to be more inorganically associated. The washability studies (analyses of specific gravity fractions of coals) indicate the potential effective removal of major portions of several trace elements, e.g., Zn, Cd, and Pb, from raw coals by conventional specific gravity methods of separation.

Several trace and minor elements have been identified as occurring in discrete mineral phases in the coals. Among these are Zn and Cd in sphalerite (ZnS), Pb in galena (PbS), and P and F in apatite $[Ca_5(PO_4)_3(F,CO_3)]$.

INTRODUCTION

Because huge tonnages of coal are burned each year for electric power generation, volatile materials, such as sulfur oxides, and the fine particulate matter emitted into the atmosphere during coal combustion are considered to be potential environmental hazards. Further, it has been clear for some time that the major chemical constituents retained in fly ash, bottom ash, and other coal combustion products may constitute long-term disposal hazards if they become soluble and enter ground- or surface-water systems. However, it has only recently become evident that the growing concern over environmental pollution will ultimately require a thorough knowledge of the elements present in coal in only trace amounts. These so-called trace elements have come under scrutiny because they are known to occur in coal (Goldschmidt, 1935, 1937) and because of the general knowledge that such elements as As, Be, Cd, Hg, and Pb are toxic to plant and animal life at relatively low concentrations. Many trace elements are now being considered not only as potential environmental pollutants, but also as poisons of costly catalysts in certain of the proposed coal gasification and liquefaction schemes.

It has therefore become imperative to develop accurate and reliable data on the amount of these elements present in coal, on their distribution and mode of occurrence, and on their volatility during combustion of the coal. Only with the development of a sufficiently large fund of such data will the general public and the agencies with the responsibility of protecting the environment be in a position to make intelligent decisions concerning utilization of coal.

The chemical nature of coal ash has been amply summarized in recent review articles (Francis, 1961; Ode, 1963; Nicholls, 1968; Watt, 1968; and Magee, Hall, and Varga, 1973), which deal in part with trace elements. However, research on trace elements in coal ash has not been extensive because until now they have been of little more than academic interest and because they occur in such small amounts that their determination is both costly and difficult.

Trace element investigations in coal prior to 1970 were based on analyses of high-temperature coal ash (Deul and Annell, 1956; Zubovic, Stadnichenko, and Sheffey, 1961, 1964, 1966; Zubovic, Sheffey, and Stadnichenko, 1967; Abernethy, Peterson, and Gibson, 1969), which measure the oxides of the elements in the altered mineral matter. Although such investigations are valuable for estimating concentrations of refractory constituents, or elements of low volatility, they do not reliably measure total amounts of volatile trace elements in whole coal. In this study, we have determined not only the amounts of the trace elements present in the coals but also their volatility when the coals were ashed at both high (up to 700° C) and low (< 150° C) temperatures.

Ruch, Gluskoter, and Kennedy (1971) published whole coal Hg values for Illinois coals, and O'Gorman and Walker (1972) determined a number of trace elements in low-temperature ashes from United States coals. Ruch, Gluskoter, and Shimp (1973) reported major, minor, and trace element concentrations in 25 coals, most of them from Illinois, in which results from high- and low-temperature ashes were compared with those obtained from the whole coal.

Many of their results were verified by comparing determinations obtained by analyzing the coals by two or more independent methods.

The need for verification of trace element results has recently been emphasized (von Lehmden, Jungers, and Lee, 1974) in an EPA-NBS interlaboratory comparison study, which included both a coal sample and a fly ash sample. A wide range of values was obtained for many of the trace elements, and an urgent need for better standard samples and analytical methods was indicated.

Reports of investigations of trace element fallout from power plants (Oak Ridge, 1973; and Klein and Russell, 1973), fate of trace elements during coal gasification (Attari, 1973; and Forney et al., 1974), trace element beneficiation of coal (Capes et al., 1974), trace element concentration in fly ash (Natusch, Wallace, and Evans, 1974), and mercury mass balance in a coal-fired power plant (Kalb and Baldeck, 1973) have all appeared within the past year and are indicative of the mounting interest in trace element research.

This report contains the results of analyses for major, minor, and trace elements of 101 coals, most of them from within Illinois; however, a significant number of eastern and western coals were analyzed for comparative purposes.

The following trace elements are reported in these coals: antimony (Sb), arsenic (As), beryllium (Be), boron (B), bromine (Br), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), fluorine (F), gallium (Ga), germanium (Ge), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), mercury (Hg), phosphorus (P), selenium (Se), tin (Sn), vanadium (V), zinc (Zn), and zirconium (Zr). In addition, the major and minor elements aluminum (Al), calcium (Ca), chlorine (Cl), iron (Fe), magnesium (Mg), potassium (K), silicon (Si), sodium (Na), sulfur (S), and titanium (Ti) are reported.

The techniques used to prepare the samples for chemical analyses and the analytical methods developed for determination of many of the trace elements in coal are discussed in detail in the appendix. The appendix also includes a discussion of the results obtained by two or more analytical methods for the same element and compares the determinations for a single element on samples prepared at different ashing temperatures. As a result of such cross-checking, a high degree of confidence can be placed in the "recommended" or "best" values reported.

A partial statistical analysis of the chemical analytical data has been done, and the arithmetic mean, standard deviation, and range for each element are given. The data have also been tested for the relationships of the elements to each other, and a matrix of correlation coefficients has been generated. Many of the better correlations between elements are those to be expected from most types of geologic samples.

A second set of analytical values was determined on a series of "washed" coal samples. These samples were separated into specific gravity fractions and each fraction was analyzed for most of the same major, minor, and trace elements as were the whole coal samples. The results of the analyses of these samples are of special value for two purposes. First, they demonstrate which of the elements can be removed from the coals by specific gravity techniques and the amount of each element that can be so removed. The second use for such data is to indicate the mode of occurrence of an element in the coal—to indicate whether it is in organic or inorganic combination and, if in inorganic combination, to suggest with which group of minerals it is most likely to be associated.

The total amount of data reported here is very large, and the complete geologic interpretation of these data requires more time than is available before the publication of this report. The areal and stratigraphic distributions of the trace elements in Illinois coals and the paleoenvironmental and diagenetic significances of these distributions will be reported in the near future.

The Illinois State Geological Survey expects to continue investigations of trace elements in coal, extending the closely spaced sample grid into that part of the Illinois Basin which lies in Indiana and Kentucky, and including more samples from the eastern and western United States.

Acknowledgment

The work on which this publication is based was performed under Contract No. 68-02-0246 and Grant No. R-800059 from the U.S. Environmental Protection Agency, Clean Fuels and Energy Branch, Control Systems Laboratory, Research Triangle Park, North Carolina. This partial financial support for this investigation from the Environmental Protection Agency is gratefully acknowledged.

TYPE AND SOURCE OF COAL SAMPLES

Chemical analyses of 101 whole coal samples were made for this study. Seventy-six of the samples were composite face-channel samples collected in coal mines by Illinois State Geological Survey personnel. Each face-channel sample was cut by hand with a pick and represented the full height of the coal seam, excluding only mineral bands, partings, or nodules more than three-eighths of an inch thick. This procedure follows a long-standing practice at the Illinois State Geological Survey and is based on a technique described by Holmes (1918) in which mineral bands greater than three-eighths inch in thickness were excluded. Generally, three face-channel samples were collected in each mine, but in some mines only two could be collected. The face-channel samples were crushed to pass a one-eighth-inch screen, combined into a composite sample, and then riffled to the desired quantity.

The coal sample was comminuted further to 20 mesh (740 μm), 60 mesh (250 μm), 100 mesh (149 μm), or finer, depending on the analytical technique to be applied. In all cases, the sample was subdivided into aliquots by riffle-type sample splitters or by quartering the sample. The parts are thus considered representative of the original coal sample.

Of the 25 coal samples that were not face-channel samples, four (C-13324, C-13433, C-15943, and C-15944) were drill cores. The first two drill cores are from the Herrin (No. 6) Coal Member, and the last two are from the Davis and DeKoven Coal Members, respectively. The drill cores were treated much like a face-channel sample (omitting mineral bands more than three-eighths of an inch thick). The following 14 samples represent production from individual mines and were provided by coal companies or state or federal agencies: C-17095 and C-17243 (Belmont County, Ohio), C-17046 and C-17047 (Montana), C-17045 (Arizona), C-17098 (Cambria, Pennsylvania), C-17092 (Coshocton County, Ohio), C-17096 (Utah), C-17244 (Harrison County, Ohio), C-17099 (Marion, Pennsylvania), C-17305 (Muhlenberg, Kentucky), C-17309 (Arizona), C-17054 (Colorado), and C-17097 (Colorado). Samples C-17970 and C-18009, National Bureau of Standards (NBS) samples SRM-1632 and SRM-1630, respectively, are combinations of several West Virginia coals. Four samples, C-17304 (Clay County, Indiana), C-17307 (Henry County, Missouri), C-17245 (Jefferson County, Ohio), C-17246 (Kanawha County, West Virginia), and C-17303 (Washington County, Pennsylvania), are not raw coal samples but represent commercially washed coal from the mines. The samples were obtained by other agencies and sent to the Survey.

RESULTS OF ANALYSES OF WHOLE COAL

The results of the chemical analyses of the 101 coal samples investigated are given in tables 1 through 4. All analyses in this report are given on the "whole coal" basis and not as a percentage of ash. Table 1 lists the results of the analyses for 23 trace elements, all reported in parts per million (ppm). Table 2 consists of the major and minor element determinations on the same coals. The standard coal analyses, proximate, ultimate, and heating value, are given in table 3. In addition, table 3 contains the low-temperature ash values as well as the high-temperature ash values for each coal. Table 4 contains the results of the analyses for varieties of sulfur and two total sulfur determinations, one by the standard ASTM method and the other by X-ray fluorescence.

In all four of the tables the first 82 samples are from the Illinois Basin (Illinois, Indiana, and western Kentucky), and the last 19 are from other states. The 82 samples from the Illinois Basin are listed in stratigraphic order beginning with the oldest coal seam. Coals from Illinois are identified with the following symbols: Reynoldsburg Member (Rb), coal in Abbott Formation (AF), Delwood Member (DW), Murphysboro Member (MU), Davis Member (DV), DeKoven Member (DK), coal in Mattoon Formation (MF), and the numbers 1, 2, 4, 5, 6, and 7 for the following coal members: Rock Island (No. 1), Colchester (No. 2), Summum (No. 4), Springfield or Harrisburg (No. 5), Herrin (No. 6), and Danville (No. 7). Coals from states other than Illinois are identified by a two-letter state abbreviation. The last two samples listed are National Bureau of Standards (NBS) samples 1630 (our sample Number C-18009) and 1632 (our sample Number C-17970).

TABLE 1—TRACE ELEMENTS IN COALS
(parts per million, moisture-free whole coal)

SAMPLE NO.	COAL SEAM	AS	B	BE	BR	CD	CO	CR	CU	F	GA	GE	MO
C-13854	RB	4,0		0,7	19	<0,1	18	11	5	52	2,7	4	0,60
C-17089	RB	22,0	37	0,5	12	<0,2	4	12	6	61	3,7	1	1,10
C-16787	AF	20,0	12	1,8	22	<0,3	18	16	27	45	3,6	4	0,22
C-15678	1	7,5	137	1,9	11	0,4	11	6	11	30	1,7	10	0,10
C-16919	DW	17,0	31	2,2	19	<0,3	20	16	19	55	2,9	5	0,16
C-16408	MU	57,0	49	0,9	11	<0,4	17	7	16	83	2,7	2	0,30
C-15943	DV	3,4	33	3,4	18	<0,3	6	8	12	51	2,8	6	0,05
C-17601	DV	5,0	33	1,4	14	5,0	16	12	11	80	2,1	6	0,05
C-15944	DK	37,0	38	4,0	17	0,4	14	13	26	60	3,6	6	0,37
C-13039	IN	3,0	110	2,4	14	<0,4	5	14	16	135	3,9	6	0,06
C-17304	IN	4,8	125	3,4	13	0,7	12	30	30	70	4,9	1	0,10
C-14646	2	5,7	131	2,7	12	<0,5	9	10	30	55	4,8	14	0,27
C-14650	2	66,0		2,4	9	8,7	28	6	28	33	2,3	22	0,16
C-15863	2	73,0		3,0	13	3,8	11	7	44	41	3,5	22	0,22
C-15566	2	93,0	115	2,5	10	0,9	34	4	26	46	7,5	43	0,49
C-15331	4	19,0	43	1,1	11	0,7	9	14	20	49	2,6	9	0,19
C-15496	4	15,0	126	3,2	16	22,0	4	9	12	43	2,6	28	0,12
C-16564	4	5,5	137	2,6	23	9,2	5	9	10	39	2,6	20	0,12
C-12495	5	5,5	164	1,1	12	<0,6	2	8	12	42	1,9	9	0,09
C-13046	IN	8,0	159	1,8	14	<0,4	10	7	12	37	1,7	10	0,27
C-13983	5	3,3	119	1,2	16	0,5	5	12	9	52	2,2	5	0,04
C-14194	5	9,1	15	1,1	15	1,6	6	14	9	58	1,8	7	0,13
C-14609	5	56,0	58	0,9	17	<0,3	9	9	12	70	2,3	6	0,12
C-14735	5	7,3	70	1,2	33	0,8	6	26	9	52	1,7	6	0,22
C-14774	5	4,5	141	1,8	14	7,2	3	8	8	42	2,2	12	0,28
C-14796	5	26,0	48	1,2	22	<0,4	4	20	33	112	6,0	3	0,38
C-15012	5	32,0	79	1,3	16	1,0	13	9	10	56	2,4	5	0,10
C-15208	5	17,0	129	1,4	11	<0,5	5	11	10	52	2,0	<1	0,18
C-15384	5	7,4	40	1,2	14	<0,4	8	14	10	55	3,0	5	0,16
C-15448	5	4,1	170	1,6	12	1,0	8	10	12	143	2,9	4	0,07
C-16264	5	9,6	139	3,0	14	2,7	2	16	10	69	4,3	15	0,24
C-16729	5	32,0	75	1,0	14	<0,4	10	12	9	48	2,6	6	0,07
C-17001	5	9,4	37	1,6	16	1,3	8	30	8	44	2,0	8	0,50
C-17305	KY	14,0	60	2,6	11	0,9	17	16	16	83	2,2	8	0,24
C-17721	5	66,0	105	2,4	18	0,6	6	12	14	88	2,2	7	0,10
C-17984	5	61,0	60	1,4	18	1,5	9	10	11	74	2,3	5	0,13
C-17988	5	47,0	63	0,9	17	1,2	9	10	10	66	2,1	5	0,09
C-18040	5	3,6	126	0,8	12	1,4	4	8	7	60	1,7	2	0,03
C-12059	6	8,6		2,3	17	20,0	10	21	26	51	3,6	9	0,58
C-12831	6	4,2	106	1,4	17	<0,4	4	7	6	51	4,5	6	0,25
C-12942	6	4,2	100	0,8	14	<0,5	5	16	14	58	1,9	<1	0,18
C-13324	6	8,1	65	0,9	14	1,1	6	12	10	44	2,4	5	0,31
C-13433	6	6,5	93	0,8	20	0,3	6	12	10	75	1,6	3	0,22
C-13464	6	4,3	110	1,8	15	0,5	9	54	10	59	3,0	<1	0,21
C-13895	6	2,1	132	1,5	15	<0,5	2	12	12	69	3,3	4	0,17
C-13975	6	6,7	122	1,2	15	<0,4	7	11	14	51	3,0	4	0,08
C-14574	6	31,0		2,2	14	2,1	3	12	12	42	2,5	11	0,22
C-14613	6	4,0	138	0,8	16	2,1	15	14	16	51	2,8	2	0,18
C-14630	6	9,2	86	1,2	21	<0,3	19	12	11	52	2,6	2	0,09
C-14684	6	3,7	82	0,8	19	<0,3	5	10	8	63	2,8	<1	0,18
C-14721	6	4,6	122	1,4	17	1,8	9	16	10	60	3,5	3	0,38

Note: The first 82 samples are from the Illinois Basin (Illinois, Indiana, and western Kentucky) and are listed in stratigraphic order beginning with those from the oldest coal seam. The last 19 are from other states and are identified by two-letter state abbreviations, with the exception of the last two, which were obtained from the National Bureau of Standards (NBS).

TABLE 1—Continued

SAMPLE NO.	COAL SEAM	AS	B	BE	BR	CD	CO	CR	CU	F	GA	GE	HG
C-14830	6	4,0	195	2,4	13	< 0,4	7	12	10	47	3,5	6	0,22
C-14970	6	2,1	186	1,6	16	< 0,4	7	10	13	44	3,7	< 1	0,14
C-14982	6	2,3	159	1,0	11	< 0,4	5	9	9	54	2,6	2	0,19
C-15038	6	5,9	117	1,0	12	0,8	11	12	12	68	2,5	1	0,11
C-15079	6	11,0	171	1,8	10	< 0,5	8	17	22	58	3,8	14	0,35
C-15117	6	30,0	155	3,9	6	1,2	14	18	17	51	3,9	12	0,32
C-15125	6	9,4	216	1,6	15	7,8	2	8	8	54	1,7	18	0,21
C-15231	6	2,4	179	0,8	13	1,4	4	11	12	76	3,7	4	0,19
C-15432	6	5,7		2,5	17	< 0,4	8	14	14	58	3,0	12	0,10
C-15436	6	3,8		1,8	19	3,3	6	37	18	51	2,3	7	0,21
C-15456	6	1,7	156	1,4	15	< 0,4	5	15	11	103	3,5	1	0,09
C-15717	6	1,9	163	1,2	13	< 0,5	6	14	10	96	2,4	1	0,08
C-15791	6	30,0	91	1,4	20	< 0,3	10	25	14	58	2,8	5	0,12
C-15868	6	1,8	102	1,0	13	2,5	12	10	13	64	2,9	2	0,08
C-15872	6	10,0	171	1,7	11	2,2	12	16	18	50	3,6	13	0,23
C-15999	6	3,1	82	1,5	14	< 0,4	12	14	15	81	3,0	2	0,14
C-16030	6	4,5	34	2,7	15	3,4	14	26	18	58	4,6	7	0,14
C-16139	6	5,1	154	1,0	12	0,9	8	25	14	65	3,3	4	0,10
C-16265	6	10,0		2,7	52	< 0,4	15	20	14	48	4,1	26	0,17
C-16317	6	24,0	104	2,8	14	28,0	9	26	20	52	4,7	12	0,10
C-16501	6	8,7	107	0,7	15	< 0,4	9	10	12	54	3,1	< 1	0,12
C-16543	6	8,1		2,4	8	65,0	13	14	16	46	3,3	14	0,41
C-16741	6	4,2	132	1,4	13	1,8	8	20	16	44	3,3	6	0,15
C-16993	6	9,0	81	1,3	16	< 0,5	7	16	12	61	3,8	< 1	0,15
C-17016	6	3,3	196	1,2	11	< 0,5	6	11	12	68	2,9	7	0,12
C-17878	6	2,3		1,1	13	0,6	5	10	13	78	2,6	5	0,16
C-18044	6	4,6	145	1.0	13	1.5	8	13	10	64	3,1	< 1	0,04
C-15278	7	5,6		1,5	13	< 0,3	5	9	8	60	2,4	9	0,39
C-15418	IN	2,3	177	2,3	19	< 0,3	22	14	13	46	4,1	11	1,60
C-17053	7	5,8	169	1,5	13	< 0,4	6	12	8	41	2,4	10	0,10
C-17815	MF	20,0	130	4,0	13	< 0,6	7	13	14	40	5,2	11	0,08
C-17065	AZ	1,2	30	0,6	7	< 0,6	2	8	12	78	4,4	2	0,08
C-17066	MT	1,2	92	1,0	20	< 0,4	2	5	18	48	3,5	3	0,09
C-17067	MT	2,5	84	1,1	25	< 0,4	2	7	15	58	3,4	2	0,07
C-17094	CO	0,7	39	[illegible]	10	< 0,4	2	6	16	63	2,4	2	0,08
C-17096	UT	0,5		0,4	23	< 0,2	1	7	11	90	1,6	1	0,04
C-17097	CO	0,5	138	0,8	19	< 0,4	2	5	10	105	3,7	3	0,08
C-17307	MO	9,3	66	1,2	7	11,0	43	22	61	91	4,0	9	0,18
C-17309	AZ	1,3	17	0,2	4	< 0,2	7	5	22	39	1,6	2	0,06
C-17092	OH	14,0	83	1,5	8	< 0,6	5	14	22	129	4,4	6	0,15
C-17095	OH	6,7	45	0,9	12	< 0,5	8	16	12	90	3,2	< 1	0,13
C-17098	PA	27,0	9	1,1	13	< 0,5	7	18	26	72	5,5	< 1	0,28
C-17099	PA	19,0	38	0,6	17	< 0,4	10	11	15	67	2,9	1	0,16
C-17243	OH	13,0	78	1,4	11	< 0,6	20	16	20	71	3,6	4	0,16
C-17244	OH	25,0	59	1,6	17	< 0,4	33	23	28	88	3,9	< 1	0,46
C-17245	OH	35,0	68	1,4	14	< 0,4	28	10	12	51	3,0	5	0,26
C-17246	WV	5,1	9	2,6	26	< 0,2	16	12	26	50	4,6	2	0,08
C-17303	PA	6,7	5	1,3	23	< 0,2	12	18	11	58	4,2	2	0,14
C-17970	NDB	5,7	43	1,7	20	< 0,4	11	22	23	81	4,5	2	0,18
C-18009	NDB	19,0	5	1,0	29	< 0,2	6	8	16	25	1,1	1	0,14

TABLE 1—Continued

SAMPLE NO.	COAL SEAM	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR
C-13054	RB	6		22	53	11	1.1	0.4		20	19	19
C-17089	RB	16	<1	20	183	59	1.5	2.2	1	20	20	
C-16787	AF	7	<2	39	65	22	1.2	2.7	3	26	20	83
C-15678	1	44	10	14	48	38	0.4	3.2	<1	16	204	84
C-16919	DW	9	<1	32	56	46	1.2	3.2	1	40	21	12
C-16408	MU	13	6	26	195	40	2.0	2.3	<2	31	26	
C-15943	DV	15	3	18	34	64	0.6	1.9	2	21	25	60
C-17601	UV	17	7	33	118	52	0.8	1.8	<2	31	61	26
C-15944	DK	10	3	27	144	192	1.4	3.0	2	36	178	31
C-13039	IN	32	4	15	49	10	0.4	1.7	30	37	10	33
C-17306	IN	74	5	24	125	7	0.6	2.7	5	39	101	70
C-14646	2	42	5	16	14	25	2.8	1.7	3	33	46	111
C-14650	2	18		36	40	178	5.7	1.1		22	926	
C-15263	2	12	2	40	24	96	5.7	2.0	<3	23	425	
C-15566	2	90	6	65	29	218	8.9	1.8	<1	19	218	
C-15331	4	28	14	15	24	103	2.7	2.5	<2	31	58	22
C-15496	4	66	<1	27	12	36	5.2	1.6	<1	22	811	47
C-16564	4	170	9	13	30	52	1.2	1.6	<5	33	571	
C-12495	5	86	6	10	21	6	0.6	1.3	51	20	17	26
C-13046	IN	46	6	11	25	8	1.2	2.2	7	34	29	
C-13983	5	26	16	14	80	16	0.5	1.9	<2	29	17	116
C-14194	5	161	18	25	11	45	0.4	1.5	<2	78	480	54
C-14609	5	52	5	24	162	114	2.4	1.1	<4	27	68	16
C-14735	5	22	19	17	80	52	1.6	3.0	<2	76	171	48
C-14774	5	100	7	9	29	28	0.9	1.9	<4	27	958	22
C-14796	5	43	3	21	320	24	0.8	1.7	4	35	63	
C-15012	5	83	9	27	10	59	1.2	2.1	3	31	181	27
C-15208	5	181	4	16	30	12	1.8	2.3	<5	34	40	28
C-15384	5	62	9	16	<10	40	2.6	1.6	3	47	33	133
C-15448	5	32	24	26	159	10	0.3	3.2	3	32	342	
C-16264	5	21	5	22	110	51	0.8	1.5	<2	22	159	52
C-16729	5	76	4	19	69	50	0.9	1.8	<2	40	24	
C-17001	5	22	14	17	48	56	2.5	3.3	7	62	170	70
C-17305	KY	56	11	11	71	11	1.6	2.6	<2	39	95	
C-17721	5	10	2	21	339	40	1.5	1.5	4	25	14	
C-17984	5	21	3	24	149	116	2.3	1.4	<1	31	344	62
C-17988	5	62	3	22	112	87	1.2	1.7	<4	28	268	
C-18040	5	93	6	8	42	4	0.4	1.7	<4	27	146	
C-12059	6	87	11	32	<10	40	1.4	3.2	22	43	3173	61
C-12831	6	28	11	14	29	7	0.3	1.3	<4	31	82	53
C-12942	6	53	8	14	7	20	0.5	1.6	<2	46	99	
C-13324	6	19	29	16	5	34	0.5	2.1	<2	38	333	82
C-13633	6	23	3	21	118	14	1.0	1.4	<1	28	52	
C-13464	6	69	11	16	48	10	1.1	2.3	2	50	29	103
C-13895	6	54	8	12	<10	6	0.3	1.9	5	17	28	65
C-13975	6	44	4	26	26	18	0.6	2.1	<4	32	39	25
C-14574	6	17	<1	18	264	50	1.6	1.6	7	18	298	16
C-14613	6	26	2	25	55	12	0.6	1.7	<3	34	328	
C-14630	6	27	2	23	135	21	0.7	1.6	<3	32	60	79
C-14684	6	30	3	12	18	11	0.2	1.8	2	20	30	40
C-14721	6	65	4	17	23	11	0.7	1.4	<2	28	270	83

TABLE 1—Concluded

SAMPLE NO.	COAL SEAM	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR
C-14838	6	80	9	16	66	5	0,3	1,0	< 4	28	49	91
C-14970	6	72	6	13	22	5	0,3	1,7	< 2	19	23	30
C-14982	6	41	15	14	42	6	0,4	1,9	< 2	34	152	83
C-15038	6	42	5	36	53	12	0,4	1,3	< 4	32	99	68
C-15079	6	69	11	34	41	116	2,7	2,3	< 7	55	46	44
C-15117	6	72	6	25	28	206	2,6	2,0	2	27	117	36
C-15125	6	150	7	10	9	24	0,8	1,1	< 5	35	616	85
C-15231	6	39	9	16	28	6	0,4	1,6	< 4	34	209	28
C-15432	6	160	<1	36	21	18	2,4	1,5	< 4	32	144	
C-15436	6	21	10	20	28	5	0,4	1,6	< 4	47	360	
C-15456	6	25	13	14	12	7	0,3	1,9	4	26	105	45
C-15717	6	48	14	16	76	5	0,4	2,1	< 4	45	47	
C-15791	6	23	2	22	8	44	1,1	2,6	< 2	26	255	26
C-15868	6	37	3	22	72	11	0,6	1,7	< 3	22	183	
C-15872	6	181	12	36	77	75	2,2	2,0	< 5	42	312	22
C-15999	6	12	15	18	10	24	0,4	1,3	< 2	36	86	88
C-16030	6	15	19	42	40	52	1,0	2,0	2	28	1599	39
C-16139	6	61	14	36	57	4	1,4	7,7	<5	46	89	
C-16265	6	67	10	28	35	65	2,0	1,7	13	34	13	
C-16317	6	67	9	30	21	72	4,3	2,4	<4	32	2668	20
C-16501	6	22	6	14	18	18	0,4	2,1	<5	27	22	115
C-16543	6	92	15	25	24	37	1,7	2,1	<4	32	5350	115
C-16741	6	70	12	33	39	16	0,7	4,7	<4	42	291	47
C-16993	6	43	4	26	66	34	0,3	2,0	<6	54	46	
C-17016	6	36	9	20	22	6	0,3	2,2	<2	20	39	31
C-17278	6	25	20	16	31	5	0,6	1,4	<2	30	100	56
C-18044	6	34	7	25	31	10	0.4	2.2	< 4	33	71	36
C-15278	7	78	5	8	68	9	0,2	0,9	< 3	27	137	42
C-15418	IN	11	<1	68	100	18	4,4	0,7	4	38	97	40
C-17053	7	77	5	14	17	9	0,4	1,2	2	25	38	
C-17215	MF	63	10	12	99	10	0,9	2,5	10	48	46	
C-17045	AZ	22	< 1	7	109	6	0,6	1,6	< 5	26	7	
C-17046	MT	101	30	4	48	7	0,9	0,8	< 5	14	12	169
C-17047	MT	88	8	6	39	7	0,9	0,8	15	18	10	0
C-17054	CO	16	2	8	10	6	0,6	2,3	8	20	12	41
C-17096	UT	< 8	1	4	80	4	0,2	1,2	< 2	11	13	74
C-17097	CO	12	2	3	400	5	0,2	1,0	5	14	7	25
C-17307	MO	108	14	80	248	102	1,2	2,9	<10	40	1444	40
C-17309	AZ	6	2	5	125	4	0,3	1,2	<2	17	15	
C-17092	BM	55	11	11	86	11	0,6	3,2	<3	42	40	42
C-17095	BM	27	< 4	16	94	4	0,6	3,0	<4	46	26	30
C-17098	PA	14	2	16	94	10	0,9	6,6	8	52	35	43
C-17099	PA	18	8	16	133	8	0,3	2,2	2	38	27	
C-17243	BM	48	6	16	179	6	1,2	2,0	<6	28	31	
C-17244	BM	29	4	22	70	10	1,5	6,3	<5	49	38	
C-17245	BM	12	5	12	64	6	1,0	1,8	3	24	30	48
C-17246	WV	9	1	19	16	7	1,3	3,1	6	28	22	8
C-17303	PA	12	1	20	104	7	0,9	1,3	5	46	21	
C-17970	NBB	39	5	20	118	23	3,0	2,8	10	50	42	
C-18009	NBB	6	2	10	17	4	0,6	2,0	6	24	6	21

TABLE 2—MAJOR AND MINOR ELEMENTS IN COALS
(percent, moisture-free whole coal)

SAMPLE NO.	COAL SEAM	AL	CA	CL	FE	K	MG	NA	SI	TI
C-13054	RB	0.60	0.38	0.30	1.90	0.04	0.03	0.009	0.58	0.02
C-17089	RB	0.67	0.39	0.24	0.68	0.08	0.02	0.004	0.74	0.03
C-16787	AF	1.07	0.24	0.19	1.73	0.15	0.02	0.016	1.64	0.08
C-19678	1	0.66	1.02	0.02	3.00	0.04	0.03	0.030	0.94	0.02
C-16919	DW	1.34	0.18	0.15	1.44	0.24	0.04	0.018	2.38	0.08
C-16408	MU	1.02	0.23	0.10	3.51	0.13	0.03	0.007	1.41	0.05
C-15943	DV	1.14	0.14	0.28	2.19	0.18	0.04	0.017	2.09	0.07
C-17601	DV	1.16	0.17	0.18	2.38	0.18	0.04	0.013	2.24	0.06
C-15944	DR	1.28	0.14	0.31	2.19	0.18	0.04	0.010	2.04	0.07
C-13039	IW	1.18	0.87	0.37	2.07	0.18	0.02	0.149	1.80	0.06
C-17304	IW	1.72	0.52	0.02	2.05	0.21	0.06	0.021	3.24	0.07
C-14646	2	1.20	0.49	0.04	2.84	0.17	0.05	0.018	2.09	0.05
C-14690	2	0.63	0.53	0.02	4.06	0.08	0.02	0.005	1.07	0.04
C-15263	2	1.01	0.10	0.02	2.65	0.14	0.04	0.014	1.65	0.05
C-15966	2	0.43	0.93	0.01	2.81	0.06	0.01	0.022	0.88	0.02
C-15331	4	0.84	0.67	0.16	2.42	0.19	0.01	0.018	2.04	0.05
C-15496	4	1.04	0.42	0.02	1.92	0.15	0.04	0.018	2.21	0.06
C-16568	4	1.05	0.37	0.03	3.87	0.16	0.04	0.037	2.88	0.08
C-12495	5	0.73	0.89	0.13	2.63	0.10	0.04	0.089	2.24	0.04
C-13046	IN	0.71	0.65	0.23	2.40	0.11	0.04	0.078	1.97	0.04
C-13903	5	1.11	0.63	0.02	2.89	0.17	0.04	0.035	2.67	0.07
C-14194	5	0.97	2.18	0.15	2.48	0.16	0.17	0.011	2.55	0.06
C-14609	5	1.05	0.94	0.16	1.91	0.16	0.06	0.016	1.99	0.07
C-14735	5	1.08	0.78	0.33	1.96	0.15	0.03	0.098	2.68	0.06
C-14774	5	1.00	1.31	0.02	1.71	0.14	0.05	0.025	2.68	0.05
C-14796	5	1.38	0.46	0.03	0.89	0.27	0.06	0.026	2.08	0.08
C-15012	5	1.15	1.07	0.09	1.92	0.17	0.04	0.017	2.32	0.07
C-15808	5	0.94	1.60	0.21	1.87	0.11	0.01	0.119	2.50	0.05
C-15384	5	1.04	0.61	0.23	2.69	0.17	0.11	0.036	2.56	0.06
C-15448	5	2.77	0.48	0.03	2.68	0.13	0.05	0.020	2.77	0.07
C-16264	5	0.92	0.56	0.01	2.05	0.15	0.04	0.051	1.92	0.05
C-16789	5	1.02	1.23	0.39	2.12	0.15	0.04	0.033	2.27	0.06
C-17001	5	0.86	0.82	0.27	2.76	0.14	0.02	0.048	2.08	0.06
C-17305	KY	1.25	1.18	0.03	2.54	0.22	0.05	0.084	2.63	0.06
C-17721	5	1.21	0.21	0.31	1.69	0.21	0.05	0.071	2.07	0.07
C-17984	5	1.11	0.37	0.20	1.66	0.17	0.03	0.016	2.07	0.07
C-17988	5	1.16	1.22	0.30	1.56	0.17	0.08	0.027	2.30	0.07
C-18040	5	1.14	1.06	0.03	1.59	0.15	0.05	0.020	2.77	0.05
C-12059	6	1.29	0.62	0.03	1.74	0.14	0.04	0.065	2.18	0.06
C-12031	6	1.20	0.93	0.28	1.50	0.16	0.04	0.060	2.45	0.06
C-12942	6	1.16	1.68	0.20	2.45	0.17	0.05	0.022	2.48	0.07
C-13384	6	1.11	0.27	0.31	2.02	0.17	0.05	0.045	2.20	0.06
C-13433	6	1.01	0.30	0.48	1.42	0.16	0.05	0.041	1.95	0.06
C-13464	6	1.18	0.50	0.33	2.34	0.17	0.06	0.190	2.65	0.05
C-13095	6	1.29	0.50	0.04	2.94	0.15	0.04	0.029	2.77	0.06
C-13975	6	1.39	0.70	0.03	1.79	0.18	0.05	0.012	2.81	0.07
C-14574	6	1.20	0.30	0.10	1.41	0.16	0.04	0.043	1.91	0.06
C-14613	6	1.41	0.45	0.54	1.09	0.17	0.04	0.145	2.39	0.08
C-14630	6	1.31	0.54	0.47	0.95	0.18	0.04	0.099	2.31	0.07
C-14684	6	1.11	0.56	0.42	1.72	0.15	0.02	0.108	2.10	0.06
C-14721	6	1.04	0.66	0.02	1.75	0.15	0.03	0.021	2.00	0.06

Note: The first 82 samples are from the Illinois Basin (Illinois, Indiana, and western Kentucky) and are listed in stratigraphic order beginning with those from the oldest coal seam. The last 19 are from other states and are identified by two-letter state abbreviations, with the exception of the last two, which were obtained from the National Bureau of Standards (NBS).

TABLE 2—Concluded

SAMPLE NO.	COAL SEAM	AL	CA	CL	FE	K	MG	NA	SI	TI
C-14838	6	1,31	0,73	0,16	1,78	0,18	0,06	0,138	3,03	0,08
C-14970	6	1,00	0,80	0,14	1,72	0,13	0,03	0,096	1,89	0,05
C-14982	6	1,40	0,97	0,09	1,58	0,17	0,06	0,072	2,89	0,06
C-15038	6	1,20	0,68	0,11	1,22	0,21	0,04	0,034	2,65	0,07
C-15079	6	3,04	0,52	0,01	3,26	0,24	0.11	0,037	4,63	0,15
C-15117	6	1,31	0,76	0,01	2,72	0,16	0,05	0,013	2,17	0,07
C-15125	6	1,01	1,76	0,03	1,89	0,14	0,04	0,046	2,78	0,06
C-15231	6	1,36	0,90	0,14	1,83	0,17	0,07	0,091	2,87	0,06
C-15432	6	1,55	1,14	0,20	1,35	0,15	0,03	0,097	3,12	0,09
C-15436	6	1,27	0,24	0,10	1,50	0,17	0,06	0,112	2,79	0,06
C-15496	6	1,38	0,67	0,01	1,43	0,20	0,05	0,032	2,70	0,07
C-15717	6	1,30	1,91	0,03	1,77	0,14	0,05	0,031	2,79	0,06
C-15791	6	1,50	0,41	0,52	1,36	0,20	0,06	0,140	2,56	0,07
C-15868	6	1,30	0,91	0,54	0,48	0,17	0,03	0,101	2,38	0,06
C-15872	6	1,65	1,32	0,01	2,14	0,16	0,09	0,018	2,72	0,07
C-15999	6	1,57	0,21	0,07	1,95	0,22	0,05	0,015	3,01	0,08
C-16030	6	1,23	0,21	0,18	1,91	0,20	0,05	0,015	2,47	0,07
C-16139	6	1,33	0,71	0,22	1,78	0,16	0,06	0,127	2,95	0,06
C-16265	6	1,42	1,28	0,02	1,86	0,12	0,06	0,019	2,25	0,06
C-16317	6	1,12	0,73	0,02	1,57	0,17	0,05	0,017	2,40	0,07
C-16501	6	1,32	0,72	0,43	1,99	0,16	0,04	0,119	2,64	0,06
C-16543	6	1,51	2,67	0,03	1,59	0,14	0,04	0,033	2,46	0,08
C-16741	6	1,40	1,09	0,02	1,80	0,16	0,04	0,013	2,44	0,07
C-16993	6	1,05	0,63	0,12	2,96	0,20	0,07	0,032	3,47	0,12
C-17016	6	1,40	0,43	0,13	4,32	0,11	0,05	0,121	2,66	0,08
C-17278	6	1,41	0,34	0,07	2,24	0,18	0,05	0,116	3,13	0,07
C-18044	6	1,65	0,49	0,02	1,64	0,80	0,06	0,015	3,63	0,08
C-15278	7	1,13	0,82	0,11	1,65	0,17	0,05	0,048	2,17	0,06
C-15418	IN	1,53	0,05	0,03	1,00	0,30	0,06	0,028	3,27	0,09
C-17053	7	1,15	1,01	0,17	2,34	0,18	0,05	0,082	2,30	0,05
C-17215	MF	1,91	0,69	0,02	3,17	0,20	0,07	0,038	3,11	0,10
C-17045	AZ	1,76	1,44	0,01	0,49	0,06	0,09	0,027	3,11	0,08
C-17046	MT	1,71	1,65	0,02	0,60	0,11	0,23	0,020	3,09	0,06
C-17047	MT	1,63	1,49	0,01	1,23	0,18	0,25	0,019	3,10	0,06
C-17056	CB	2,23	0,60	0,03	0,91	0,06	0,03	0,013	3,40	0,13
C-17096	UT	0,72	0,93	0,03	0,48	0,02	0,03	0,200	1,99	0,06
C-17097	CB	1,82	0,62	0,02	0,34	0,12	0,09	0,028	3,38	0,06
C-17307	NB	2,37	1,16	0,06	3,07	0,43	0,10	0,072	6,09	0,08
C-17309	AZ	0,73	2,47	0,02	0,55	0,02	0,07	0,089	1,25	0,05
C-17092	BM	1,18	0,87	0,37	2,32	0,12	0,02	0,061	1,80	0,06
C-17095	BM	2,46	0,30	0,04	2,45	0,27	0,07	0,023	4,50	0,11
C-17098	PA	2,66	0,35	0,07	1,06	0,38	0,06	0,030	3,96	0,15
C-17099	PA	1,53	0,25	0,08	2,01	0,15	0,04	0,028	2,52	0,08
C-17243	BM	1,75	0,76	0,05	2,53	0,27	0,09	0,035	3,83	0,08
C-17244	BM	1,81	0,30	0,22	1,79	0,29	0,05	0,036	3,20	0,10
C-17245	BM	1,24	0,11	0,10	2,60	0,15	0,04	0,023	2,51	0,06
C-17246	NV	1,14	0,11	0,19	0,54	0,15	0,02	0,022	1,81	0,08
C-17303	PA	1,14	2,57	0,12	0,93	0,13	0,04	0,028	2,01	0,07
C-17970	NBB	2,21	0,70	0,10	1,11	0,33	0,11	0,039	3,98	0,11
C-18009	NBB	0,53	0,07	0,22	1,04	0,08	0,02	0,032	0,72	0,05

TABLE 3—PROXIMATE AND ULTIMATE ANALYSES OF COALS (percent of whole coal, except for Btu values)

SAMPLE NO.	COAL SEAM	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	S	HTA	LTA
C-13054	MB	2.1	4.2	40.4	55.0	4.6	14362	79.94	5.76	1.83	5.98	4.56	5.82
C-17089	MB											3.20	6.17
C-16787	AF	4.4	6.7	32.0	61.0	7.1	13794	77.72	4.61	1.43	7.32	7.06	9.84
C-15678	1	13.2	14.8	44.1	45.6	10.3	12952	71.69	4.98	1.15	6.75	10.29	14.78
C-16919	DH	6.3	9.1	35.0	56.7	8.2	13800	75.63	4.93	1.50	6.67	8.24	11.00
C-16408	MU	3.9	5.3	37.0	51.8	11.2	12990	71.21	4.91	1.35	6.63	11.26	16.61
C-15943	DV	1.8	3.1	37.7	51.8	10.5	13392	74.53	5.05	1.27	4.27	10.55	13.41
C-17601	DV		1.6	36.3	52.7	11.1	13112	70.91	5.01	1.26	7.95	11.06	14.35
C-15944	DK	1.6	2.9	37.1	53.0	9.9	13517	74.92	5.09	1.44	5.44	9.91	14.59
C-13039	IN	6.3	10.2	43.7	45.4	10.9	12927	71.28	5.64	1.16	7.05	10.85	14.29
C-17304	IN		2.6	41.3	45.7	13.0		67.07	5.10	1.20	9.52	12.98	16.25
C-14646	2	10.8	12.9	44.5	44.5	11.0	12829	71.70	5.43	1.10	5.96	10.91	19.00
C-14650	2	12.1	14.5	42.9	47.6	9.5	12951	72.73	5.07	1.29	6.26	9.46	14.44
C-15263	2	10.5	13.9	41.0	51.0	8.0	13108	73.24	5.34	1.37	6.97	7.98	12.05
C-15566	2	9.0	11.2	43.5	46.4	10.1	13042	72.33	4.86	1.43	6.61	10.12	14.01
C-15331	4	2.2	4.1	38.4	47.3	14.3	12387	68.23	5.04	1.42	5.46	14.26	16.60
C-15496	4	10.7	14.7	45.5	45.3	9.2	12996	72.06	5.13	1.36	6.56	9.22	12.31
C-16564	4	7.3	12.5	45.8	44.2	10.0	12920	70.61	5.22	1.18	9.18	10.01	17.13
C-12495	5	8.7	13.4	42.5	46.8	10.7	12466	69.98	4.94	1.20	6.87	10.66	23.93
C-13046	IN	7.5	11.4	43.1	46.0	10.9	13096	70.43	5.13	1.39	7.48	10.88	16.10
C-13983	5	7.4	9.9	40.5	48.9	10.6	12736	70.76	5.30	1.26	7.01	10.61	16.92
C-14194	5	3.1	4.2	31.9	54.6	13.5	12973	72.20	5.07	1.33	4.15	13.54	17.85
C-14609	5	5.5	7.8	36.3	53.2	10.5	13137	73.20	5.22	1.20	7.06	10.40	12.65
C-14735	5	5.3	7.0	39.4	48.5	12.1	12724	71.18	5.15	1.08	6.56	12.06	16.51
C-14774	5	1.4	4.6	42.1	45.1	12.8	12405	70.31	4.91	1.19	7.09	12.82	16.48
C-14796	5	5.9	7.9	34.3	55.4	10.3	13000	74.60	5.16	1.52	7.05	10.33	12.62
C-15012	5	3.8	5.2	37.2	51.3	11.5	12873	71.06	5.11	1.36	7.10	11.42	15.98
C-15808	5	12.0	14.7	41.7	43.5	14.8	11973	67.18	5.01	1.43	7.55	14.77	20.0
C-15384	5	2.8	4.1	36.9	50.9	12.2	12997	71.94	5.06	1.70	5.19	12.21	16.40
C-15448	5	5.6	8.7	40.2	47.1	12.7	12390	68.68	5.10	1.35	7.08	12.64	17.77
C-16264	5	13.6	15.8	43.3	44.3	12.4	12480	68.99	4.88	1.14	7.94	12.53	15.87
C-16729	5	4.5	7.6	37.0	50.8	12.2	12728	71.23	4.66	1.48	7.36	12.16	16.01
C-17001	5	4.1	5.9	39.5	48.7	11.8	12947	71.57	5.03	1.48	6.00	11.79	16.01
C-17305	KY		3.1	37.9	48.8	13.3		66.86	4.94	1.15	9.86	13.29	17.86
C-17721	5	10.3	12.2	38.9	53.1	8.0	13326	73.49	4.81	1.46	9.98	8.00	10.99
C-17984	5	4.6	6.7	36.3	54.5	9.2	13276	74.20	4.99	1.84	7.78	9.16	10.66
C-17988	5	4.4	6.1	37.4	52.2	10.5	13087	73.46	5.00	1.61	7.10	10.47	14.28
C-18040	5	7.6	9.4	40.9	46.7	12.4	12456	70.27	4.93	1.36	7.17	12.40	15.40
C-12059	6	11.5	16.0	40.7	49.1	10.2	12616						10.05
C-12831	6	5.6	7.9	38.0	51.5	10.5	12895	72.16	4.99	1.55	6.22	10.48	14.08
C-12942	6	7.9	10.7	37.1	50.3	12.6	12621	69.91	5.00	1.49	7.13	12.55	17.55
C-13324	6		4.0	37.6	51.0	11.4	12779	70.76	4.85	1.30	7.45	11.34	14.78
C-13433	6	6.0	8.7	36.6	54.0	9.4	13060	73.33	5.09	1.39	7.71	9.45	11.10
C-13464	6	4.3	9.5	38.1	49.2	12.7		66.08	4.55	1.09	13.52	12.71	17.60
C-13895	6	5.4	10.5	42.6	44.5	12.9	12303	67.84	4.79	1.26	6.64	12.90	16.71
C-13975	6	6.8	9.7	36.6	51.8	11.6	12729	71.16	5.19	1.47	6.10	11.54	16.29
C-14574	6	10.2	13.5	43.6	49.0	7.4	13480	74.72	5.68	1.34	6.74	7.34	10.36
C-14613	6	7.1	10.7	38.2	52.7	9.1	13027	73.42	5.31	1.62	9.16	9.06	10.69
C-14630	6	7.1	10.4	36.4	55.0	8.6	13162	73.72	4.81	1.60	10.09	8.60	10.48
C-14684	6	6.0	8.5	38.2	51.8	10.0	12934	74.49	5.13	1.48	6.18	9.94	12.31
C-14721	6	7.9	10.8	38.6	51.8	9.6	12547	68.25	4.67	1.19	12.94	9.62	13.78

Note: The first 82 samples are from the Illinois Basin (Illinois, Indiana, and western Kentucky) and are listed in stratigraphic order beginning with those from the oldest coal seam. The last 19 are from other states and are identified by two-letter state abbreviations, with the exception of the last two, which were obtained from the National Bureau of Standards (NBS). All values are on a moisture-free, whole coal basis except for air-dry loss (ADL) and moisture (MOIS).
Other abbreviations: volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

TABLE 3—Concluded

SAMPLE NO.	COAL SEAM	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	O	HTA	LTA
C-14838	6	11,8	14,4	43,3	44,6	12,1	12465	69,49	4,98	1,27	7,91	12,10	15,47
C-14970	6	12,2	14,7	40,3	48,1	11,6	12619	69,25	4,85	1,10	8,90	11,65	15,68
C-14982	6	8,4	10,9	40,5	46,9	12,6	12255	68,57	4,88	1,15	9,03	12,67	14,94
C-15038	6	6,3	7,7	35,4	54,1	10,5	13005	73,76	5,14	1,33	7,67	10,56	13,33
C-15079	6	12,6	16,7	38,1	46,6	15,3	11900	66,26	4,88	1,04	8,54	15,31	20,66
C-15117	6	13,3	17,3	40,7	45,7	13,6	12074	67,44	5,00	0,93	8,82	13,60	15,88
C-15125	6	12,8	15,6	43,0	44,0	13,0	12220	68,68	4,99	1,07	8,72	13,07	19,07
C-15231	6	7,9	10,8	42,1	45,5	12,4	12222	68,09	5,01	1,43	8,71	12,45	15,41
C-15432	6	11,5	16,5	40,0	47,8	12,2	12438	70,58	4,63	1,70	9,16	12,19	13,97
C-15436	6	9,5	14,6	44,4	45,5	10,1	12442	68,97	5,12	1,39	11,08	10,11	14,49
C-15456	6	5,9	9,3	40,5	47,1	12,4	12274	69,23	4,72	1,54	7,64	12,42	15,37
C-15717	6	8,6	10,8	42,3	45,5	12,2	12449	69,11	4,76	1,11	8,68	12,15	17,71
C-15791	6	7,1	9,2	35,8	53,9	10,3	13008	72,92	4,96	1,75	8,15	10,34	12,94
C-15868	6	5,6	10,2	36,8	54,3	8,9	13290	75,13	4,90	1,52	6,77	8,83	10,56
C-15872	6	10,1	15,8	42,0	43,5	14,5	12109	67,70	4,63	1,04	8,51	14,44	19,69
C-15999	6	6,1	7,3	38,0	49,6	12,4	12470	69,49	4,54	1,27	6,96	12,43	15,09
C-16030	6	1,9	3,2	37,7	50,3	12,0	13140	71,96	4,83	1,35	6,44	11,92	14,26
C-16139	6	10,5	13,7	41,2	44,7	14,1	12050	66,25	4,59	1,23	9,01	14,08	18,69
C-16265	6	15,6	18,2	41,4	49,1	9,5	12810	71,79	4,97	1,11	9,43	9,50	14,56
C-16317	6	7,2	13,0	39,4	48,6	12,0	12400	69,97	4,58	1,25	8,95	12,00	17,89
C-16501	6	5,7	8,3	38,3	51,4	10,3	12980	72,06	5,08	1,56	8,61	10,32	15,55
C-16543	6	9,4	17,0	43,0	45,1	11,9	12380	68,71	5,07	1,11	10,02	11,94	16,19
C-16741	6	12,0	16,0	43,3	43,8	12,9	12455	69,53	4,91	1,10	8,02	12,89	15,73
C-16993	6	0,0	5,5			16,0	11562	64,57	4,19	1,39	9,67	16,04	20,65
C-17016	6	16,7	23,7	39,4	47,5	13,1		62,69	4,55	1,07	12,96	13,09	19,69
C-17278	6	9,6	13,9	43,6	46,1	10,3	12510						14,05
C-18044	6	8,8	10,7	39,4	48,2	12,4	12348	63,10	4,99	1,39	14,36	12,37	17,48
C-15278	7	9,5	11,9	43,5	45,5	11,0	12630	69,87	4,92	1,54	8,76	10,93	12,41
C-15418	IN	9,3	15,1	35,1	54,7	10,2		71,01	4,82	1,46	11,33	10,21	10,15
C-17053	7	8,9	12,8	46,4	42,5	11,1	12850	71,06	5,06	1,33	7,70	11,08	13,95
C-17215	MF	6,2	10,6	43,4	41,3	15,3	11908	65,30	5,02	1,60	8,68	15,27	21,94
C-17085	AZ		7,1	44,9	41,5	13,6		65,83	4,73	0,96	14,36	13,65	22,65
C-17086	MT		20,1	49,6	34,6	15,8		63,32	4,08	0,90	14,79	15,83	14,86
C-17087	MT		20,7	52,7	35,4	11,9		66,26	4,26	0,91	15,37	11,98	16,54
C-17054	CB		2,2	32,8	54,9	12,3		72,57	4,58	1,06	8,77	12,27	14,01
C-17096	UT		2,2	45,2	47,1	7,7		73,84	5,79	1,23	10,79	7,72	7,79
C-17097	CB		8,9	45,6	43,5	10,8		67,75	4,76	1,46	14,64	10,83	15,19
C-17307	MB		2,2	36,3	37,9	25,8		55,23	4,03	0,78	7,64	25,85	31,70
C-17309	AZ		6,2	44,7	48,8	6,6		70,99	5,05	1,01	15,98	6,56	7,90
C-17092	BM		3,4	38,2	47,0	14,8		64,65	4,55	1,05	10,34	14,76	21,18
C-17095	BM		2,0	36,7	45,0	18,3		62,86	4,45	0,96	9,44	18,27	22,26
C-17098	PA		0,0	18,9	65,4	15,7				1,05		15,67	18,03
C-17099	PA		1,0	39,9	49,0	11,1		64,16	4,79	0,95	16,03	11,10	14,61
C-17263	BM		2,4	37,8	46,2	16,0		65,27	4,70	1,00	8,75	16,08	21,38
C-17264	BM		1,5	35,5	51,7	12,7		70,47	4,61	1,18	8,12	12,72	15,98
C-17265	BM		1,7	37,7	51,7	10,5		70,62	4,91	1,07	9,22	10,53	14,56
C-17266	NV		0,9	34,1	59,7	6,1		80,14	5,29	1,29	4,22	6,15	7,57
C-17303	PA		1,6	36,1	57,3	6,7		78,01	5,26	1,29	7,49	6,66	8,53
C-17970	NBS											14,28	15,64
C-18009	NBS		0,4			2,2						3,83	4,50

TABLE 4—SULFUR ANALYSES (percent, moisture-free coal)

SAMPLE NO.	COAL SEAM	ORS	PYS	SUS	TOS	SXRF
C-13854	RB	0,66	1,27	0,0	1,93	2,18
C-17089	RB	0,0	0,0	0,0	0,56	0,88
C-16787	AF	0,54	1,10	0,03	1,66	1,60
C-15676	1	2,10	3,21	0,05	5,36	4,63
C-16919	DN	0,37	0,76	0,10	1,23	1,05
C-16408	MU	1,07	3,78	0,05	4,90	3,84
C-15943	DV	1,26	3,02	0,05	4,33	2,99
C-17601	DV	1,28	2,35	0,18	3,81	3,12
C-15944	DR	0,91	2,27	0,02	3,20	3,48
C-13039	IN	1,60	2,41	0,01	4,02	3,96
C-17304	IN	2,09	1,52	0,51	4,13	3,63
C-14646	2	2,07	2,72	0,04	4,83	4,34
C-14650	2	1,32	3,38	0,11	4,81	4,27
C-15863	2	0,85	2,27	0,04	3,16	2,58
C-15566	2	1,42	3,38	0,05	4,65	4,70
C-15331	4	1,75	3,78	0,06	5,59	4,23
C-15496	4	2,34	1,28	0,05	3,67	3,96
C-16564	4	2,10	1,67	0,03	3,80	4,48
C-12495	5	1,62	2,67	0,06	4,35	4,47
C-13046	IN	1,66	3,02	0,01	4,69	4,23
C-13983	5	1,78	2,47	0,02	4,27	4,27
C-14194	5	1,29	2,26	0,08	3,63	3,16
C-14609	5	1,07	1,81	0,04	2,92	2,35
C-14735	5	1,65	2,34	0,02	4,01	3,43
C-14774	5	2,24	1,42	0,02	3,68	3,74
C-14796	5	0,58	0,76	0,02	1,36	1,46
C-15018	5	1,11	2,04	0,02	3,17	2,59
C-15208	5	2,03	1,96	0,07	4,06	3,66
C-15284	5	1,63	2,13	0,14	3,90	3,63
C-15448	5	2,26	2,56	0,12	4,94	4,43
C-16264	5	2,14	2,33	0,05	4,52	4,47
C-16789	5	0,83	2,30	0,04	3,17	2,48
C-17001	5	1,51	2,62	0,02	4,14	3,49
C-17305	KY	1,44	2,00	1,06	4,50	3,61
C-17781	5	0,88	1,37	0,01	2,26	2,01
C-17984	5	0,57	1,50	0,01	2,09	1,92
C-17988	5	0,80	1,35	0,01	2,17	1,95
C-18040	5	2,11	1,74	0,01	3,86	2,85
C-18059	6				3,14	3,55
C-12031	6	1,28	1,29	0,03	2,60	2,70
C-12942	6	1,38	2,42	0,12	3,92	3,07
C-13384	6	1,59	2,69	0,02	4,30	3,37
C-13433	6	0,85	2,17	0,01	3,03	1,87
C-13464	6	1,75	1,63	0,67	4,05	4,08
C-13895	6	2,12	2,43	0,02	4,57	4,50
C-13975	6	0,71	1,62	0,01	2,34	2,36
C-14576	6	1,20	0,94	0,04	2,18	2,18
C-14613	6	0,77	0,65	0,01	1,43	1,35
C-14630	6	0,63	0,57	0,02	1,22	1,23
C-14684	6	1,33	1,44	0,02	2,79	2,46
C-14721	6	1,94	1,76	0,03	3,73	3,24
C-14830	6	2,56	1,66	0,03	4,25	3,96
C-14970	6	2,19	2,02	0,04	4,25	4,13
C-14982	6	2,12	1,57	0,01	3,70	3,37
C-15038	6	0,53	0,99	0,01	1,53	1,32
C-15079	6	1,78	2,13	0,07	3,98	3,15
C-15117	6	1,86	2,26	0,08	4,20	3,74
C-15125	6	2,02	1,42	0,01	3,45	3,40
C-15231	6	2,59	1,69	0,03	4,31	4,12
C-15432	6	0,71	0,98	0,05	1,74	1,36
C-15436	6	1,89	1,37	0,07	3,33	4,63
C-15496	6	2,03	2,36	0,06	4,45	3,86
C-15717	6	2,56	1,59	0,04	4,19	4,11
C-15791	6	0,72	1,14	0,02	1,88	1,49
C-15868	6	0,56	0,29	0,0	0,85	0,88
C-15872	6	1,82	1,81	0,05	3,68	3,29
C-15999	6	1,44	1,79	0,08	3,31	3,04
C-16030	6	1,60	1,67	0,04	3,31	3,80
C-16139	6	2,46	2,27	0,11	4,84	4,01
C-16265	6	1,94	1,22	0,04	3,20	3,53
C-16317	6	1,95	0,97	0,33	3,25	3,22
C-16501	6	1,15	1,21	0,01	2,37	2,79
C-16543	6	1,91	1,20	0,04	3,15	3,32
C-16741	6	1,96	1,54	0,05	3,55	3,63
C-16993	6	1,50	1,75	0,90	4,15	3,67
C-17016	6	2,59	2,67	0,10	5,36	5,40
C-17278	6	3,20	1,47	0,18	4,85	5,03
C-18044	6	1,85	1,85	0,01	3,71	3,29
C-15278	7	1,65	1,60	0,10	3,35	3,27
C-15418	IN	0,42	0,56	0,02	0,98	0,79
C-17053	7	1,78	1,97	0,02	3,77	4,00
C-17215	MF	1,41	2,67	0,10	4,18	2,88
C-17045	AZ	0,31	0,10	0,02	0,44	0,34
C-17046	MT	0,56	0,53	0,02	1,11	0,80
C-17047	MT	0,70	1,16	0,02	1,88	0,98
C-17084	CO	0,49	0,31	0,02	0,83	0,87
C-17096	UT	0,40	0,24	0,04	0,69	0,66
C-17097	CO	0,46	0,07	0,02	0,55	0,57
C-17307	MO	1,84	3,65	0,98	6,47	4,02
C-17309	AZ	0,34	0,06	0,01	0,42	0,36
C-17092	BM	1,41	2,37	0,16	3,94	3,96
C-17093	BM	1,42	2,59	0,19	4,20	2,94
C-17098	PA	0,46	1,01	0,05	1,53	0,92
C-17099	PA	1,01	1,82	0,21	3,04	2,33
C-17243	BM	1,32	2,41	0,42	4,15	3,81
C-17244	BM	0,69	1,85	0,12	2,66	1,82
C-17245	BM	1,05	2,39	0,24	3,68	2,85
C-17246	WV	0,74	0,19	0,02	0,96	1,23
C-17303	PA	0,75	0,48	0,06	1,29	1,46
C-17970	NBS	0,0	0,0	0,0	0,0	1,85
C-18009	NBS	0,72	0,27	0,08	1,07	1,37

Note: The first 82 samples are from the Illinois Basin (Illinois, Indiana, and western Kentucky) and are listed in stratigraphic order beginning with those from the oldest coal seam. The last 19 are from other states and are identified by two-letter state abbreviations, with the exception of the last two, which were obtained from the National Bureau of Standards (NBS). Abbreviations: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF).

STATISTICAL ANALYSES OF ANALYTICAL DATA

As a first step in the statistical analyses of the large amount of data generated, arithmetic means, standard deviations, ranges (minimum and maximum values), and linear correlation coefficients were calculated on the trace elements, major elements, high- and low-temperature ashes, and the proximate and ultimate coal analyses for the 101 coal samples. These are summarized in tables 5 and 7. Because determinations for all variables were not reported for all samples (see appendix), a missing-data statistical analysis, called MISR (IBM-SSP) (IBM Corp., 1970, p. 34), was used in this study. This computer program identified the missing data and omitted them when calculating the statistical values. Other statistical analyses were used on parts of this study in which the data were complete as a check on the validity of the missing-data analysis and the same statistical results were obtained. This particular program was used because the output (computer print-out of means, etc.) could be modified so that it could be photographed directly; and it appears in the original form in tables 5, 6, 7, and 8.

The 101 coal samples were grouped into three geographic regions: Illinois Basin (82 samples), eastern United States (11 samples), and western United States (8 samples). Arithmetic mean values, standard deviations, ranges, and linear correlation coefficients were determined using the missing-data correlation analysis (MISR) on the trace elements, major elements, high- and low-temperature ashes, and the proximate and ultimate coal analyses for each group. Because of the small sample population in the eastern U.S. and western U.S. groups, only the statistics for the Illinois Basin are presented separately in this paper (tables 6 and 8) in addition to the data for all coals analyzed.

The trace element concentrations of Cd, Ge, Mo, and Sn were reported in some samples as "less than" values. To estimate the effects of these less than values on the statistics, the means for these four elements were calculated three different ways. First, the "less than" values were used as the accepted values (< 0.4 would be equal to 0.4) with the following means as the result: Cd = 2.53, Ge = 6.59, Mo = 7.54, and Sn = 4.79. Second, half the less than values were used as the accepted values (< 0.4 would become 0.2) with the following results: Cd = 2.44, Ge = 6.49, Mo = 7.50, and Sn = 3.70. Third, zero was used in place of the less than values (< 0.4 then equals 0.0) with the following means: Cd = 2.34, Ge = 6.39, Mo = 7.48, and Sn = 2.67. For all samples in which these four elements were not reported as less than values, the accepted value was used in the three trials. For Ge, Cd, and Mo, the difference between the various means in the three trials was less than 10 percent. Similarly, the correlation coefficients for these three trace elements did not vary significantly. Therefore, the statistics reported for these three elements on tables 5, 6, 7, and 8 were calculated using the less than value as the true value (< 0.4 equal to 0.4). The different means for tin in the three trials vary by more than 30 percent and although statistical values are shown in the various tables, the results are not thought to be highly significant.

Histograms of the distribution of trace, minor, and major elements and of the high-temperature and low-temperature ashes are given in figures 1 through 39. The data for 98 of the 101 coal samples are plotted on the histograms (omitting a weathered coal sample, C-17089, and the two NBS samples) so that the three geographic groups may be differentiated. The data from the Illinois Basin coals are plotted as unpatterned bars, those from the western United States as horizontally striped bars, and those from the eastern United States as vertically striped bars. The horizontal axis is divided into class intervals and the vertical axis represents the number of samples in each class. Those samples whose values are well beyond the last regular class interval are plotted following a break in the abscissa and are identified with a plus sign (+).

On the basis of analyses of the histograms, ranges, and standard deviations, elements can be grouped with those of similar type. Within one group, elements display a more or less normal distribution of analytical values, with small standard deviations and ranges. Included within this group are Al, Fe, F, Ga, Be, Br, B, Cr, Cu, K, Ni, Si, Ti, Se, and V. Within this group are several elements with high organic affinities (discussed later in this report and in Gluskoter, 1974), and also elements which are thought to be syngenetic and therefore were contributed to the coal early in the coal swamp history. The data obtained from the second group of samples are highly skewed, with large ranges and large standard deviations. This group includes Cd, Zn, P, As, Sb, Pb, Sn, Cl, Ge, and Hg. A number of the analyses of the elements in this group were reported as "less than" values, which contributed to the skewed distribution shown for these elements. Other elements in this group are commonly found in nature as sulfides and carbonates, which when present in coal are often the result of epigenetic mineralization and may be locally concentrated. As is the case with most geologic samples, there is also an intermediate group of elements whose analytical data present a moderate range and standard deviation, including Mg, Cu, Mn, Na, Mo, and Zr.

Coefficients resulting from the correlation of one parameter with every other parameter in the four groups (all 101 coals, coals from the Illinois Basin, eastern coals, and western coals) were tested at the 1 percent level (highly significant) using the standard F test. Correlation coefficients calculated for the coals of the eastern and western United States were found to be nearly insignificant at the 99 percent confidence level because of their small sample population and thus are not shown in this report. Correlation coefficients for the Illinois Basin coals and for all 101 samples were calculated on a sufficiently large population to be significant and demonstrate the following geochemical associations:

1) An excellent positive correlation (0.93 for coals of the Illinois Basin and also for all 101 samples) is present between Zn and Cd. Zinc is present in coals, at least in part, as ZnS (sphalerite) as was previously reported by Gluskoter, Hatch, and Lindahl (1973); cadmium has been identified as occurring in solid solution with Zn in this mineral in Illinois coals (Gluskoter and Lindahl, 1973).

2) The elements of the following group have positive correlations with each other: As, Co, Cu, Ni, Pb, and Sb. These elements are commonly found in nature as sulfides (and are included among the chalcophile elements—elements which have a strong affinity for sulfur). Germanium is postively correlated with many chalcophile elements in the Illinois Basin coals and in the 101 coal samples.

(Continued on page 31)

TABLE 5—MEAN ANALYTICAL VALUES FOR ALL 101 COALS

CONSTITUENT	MEAN		STD	MIN	MAX
AS	14,02	PPM	17,70	0,50	93,00
B	102,21	PPM	54,65	5,00	224,00
BE	1,61	PPM	0,82	0,20	4,00
BR	15,42	PPM	5,92	4,00	52,00
CD	2,52	PPM	7,60	0,10	65,00
CO	9,57	PPM	7,26	1,00	43,00
CR	13,75	PPM	7,26	4,00	54,00
CU	15,16	PPM	8,12	5,00	61,00
F	60,94	PPM	20,99	25,00	143,00
GA	3,12	PPM	1,06	1,10	7,50
GE	6,59	PPM	6,71	1,00	43,00
HG	0,20	PPM	0,20	0,02	1,60
MN	49,40	PPM	40,15	6,00	181,00
MO	7,54	PPM	5,96	1,00	30,00
NI	21,07	PPM	12,35	3,00	80,00
P	71,10	PPM	72,81	5,00	400,00
PB	34,78	PPM	43,69	4,00	218,00
SB	1,26	PPM	1,32	0,20	8,90
SE	2,08	PPM	1,10	0,45	7,70
SN	4,79	PPM	6,15	1,00	51,00
V	32,71	PPM	12,03	11,00	78,00
ZN	272,29	PPM	694,23	6,00	5350,00
ZR	72,46	PPM	57,78	8,00	133,00
AL	1,29	%	0,45	0,43	3,04
CA	0,77	%	0,55	0,05	2,67
CL	0,14	%	0,14	0,01	0,54
FE	1,92	%	0,79	0,36	4,32
K	0,16	%	0,06	0,02	0,43
MG	0,05	%	0,04	0,01	0,25
NA	0,05	%	0,04	0,00	0,20
SI	2,49	%	0,80	0,58	6,09
TI	0,07	%	0,02	0,02	0,15
ORS	1,41	%	0,65	0,31	3,09
PYS	1,76	%	0,86	0,06	3,78
SUS	0,10	%	0,19	0,01	1,06
TOS	3,27	%	1,35	0,42	6,47
SXRF	2,91	%	1,24	0,54	5,60
ADL	7,70	%	3,47	1,40	16,70
MOIS	9,05	%	5,05	0,01	20,70
VOL	39,70	%	4,27	18,90	52,70
FIXC	48,82	%	4,95	34,60	63,40
ASH	11,44	%	2,69	2,20	25,80
BTU/LB	12748,95		464,50	11562,00	14362,00
C	70,28	%	3,87	55,23	80,14
H	4,95	%	0,31	4,03	5,79
N	1,30	%	0,22	0,78	1,84
S	8,68	%	2,44	4,15	16,03
HTA	11,41	%	2,95	3,28	25,85
LTA	15,28	%	4,04	3,82	31,70

Note: Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

TABLE 6—MEAN ANALYTICAL VALUES FOR 82 COALS FROM THE ILLINOIS BASIN

CONSTITUENT	MEAN		STD	MIN	MAX
AS	14,91	PPM	18,94	1,70	93,00
B	113,79	PPM	51,72	12,00	224,00
BE	1,72	PPM	0,83	0,30	4,00
BR	15,27	PPM	5,60	6,00	52,00
CD	2,89	PPM	8,32	0,10	65,00
CO	9,15	PPM	5.76	2,00	34,00
CR	14,10	PPM	7,48	4,00	54,00
CU	14,09	PPM	6,78	5,00	44,00
F	59,30	PPM	19,79	30,00	143,00
GA	3,04	PPM	1,03	1,60	7,50
GE	7,51	PPM	7,08	1,00	43,00
HG	0,21	PPM	0.22	0,03	1,60
MN	53,16	PPM	40,98	6,00	181,00
MO	7,96	PPM	5,68	1,00	29,00
NI	22,35	PPM	10,81	8,00	68,00
P	62,77	PPM	65,66	5,00	339,00
PB	39,83	PPM	45,94	4,00	218,00
SB	1,35	PPM	1,42	0,20	8,90
SE	1,99	PPM	0,93	0,45	7,70
SN	4,56	PPM	6,64	1,00	51,00
V	33,13	PPM	11,63	16,00	78,00
ZN	313,04	PPM	749,92	10,00	5350,00
ZR	72,10	PPM	58,01	12,00	133,00
AL	1,22	%	0,37	0,43	3,04
CA	0,74	%	0,49	0,05	2,67
CL	0,15	%	0,15	0,01	0,54
FE	2,06	%	0,71	0,48	4,32
K	0,16	%	0,04	0,04	0,30
MG	0,05	%	0,02	0,01	0,17
NA	0,05	%	0,04	0,00	0,19
SI	2,39	%	0,62	0,58	4,63
TI	0,06	%	0,02	0,02	0,15
ORS	1,54	%	0,62	0,37	3,09
PYS	1,88	%	0,74	0,29	3,78
SUS	0,09	%	0,18	0,01	1,06
TOS	3,51	%	1,12	0,85	5,59
SXRF	3,19	%	1,08	0,79	5,60
ADL	7,70	%	3,47	1,40	16,70
MOIS	10,02	%	4,23	1,60	18,20
VOL	39,80	%	3,17	31,90	46,40
FIXC	48,98	%	3,92	41,30	61,00
ASH	11,28	%	1,98	4,60	16,00
BTU/LB	12748,91		464,50	11562,00	14362,00
C	70,69	%	3,11	62,49	79,94
H	4,98	%	0,26	4,19	5,76
N	1,38	%	0,20	0,93	1,84
O	8,19	%	1,84	4,15	14,36
HTA	11,18	%	2,17	3,28	16,04
LTA	15.22	%	3,22	3,82	23,53

Note: Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

TABLE 7—LINEAR REGRESSION (LEAST SQUARES) CORRELATION COEFFICIENTS

	AS	B	BE	BR	CO	CS	CR	CU	F	GA	GE	MG	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR	
AS	1.0	-0.2	0.2	-0.1	0.0	0.4	-0.1	0.3	-0.0	0.2	0.4	0.1	-0.1	-0.2	0.3	0.3	0.7	0.6	0.0	-0.1	-0.1	0.0	0.3	AS
B	-0.2	1.0	0.2	-0.2	0.3	-0.2	-0.0	-0.2	-0.0	-0.0	0.3	0.1	0.4	0.2	0.0	-0.2	-0.1	0.0	-0.1	0.1	-0.1	0.3	-0.0	B
BE	0.2	0.2	1.0	0.0	0.2	0.2	0.2	0.3	-0.1	0.4	0.5	0.1	0.2	-0.1	0.3	-0.1	0.4	0.4	0.0	0.1	0.0	0.2	0.0	BE
BR	-0.1	-0.2	0.0	1.0	-0.1	-0.1	0.1	-0.1	-0.2	-0.0	0.0	0.0	-0.1	-0.1	-0.1	0.0	-0.1	-0.0	-0.1	0.1	0.1	-0.1	-0.1	BR
CO	0.0	0.3	0.2	-0.1	1.0	0.1	0.1	0.1	-0.1	0.0	0.3	0.1	0.2	0.1	0.2	-0.1	0.1	0.2	0.0	0.0	-0.0	0.9	-0.0	CO
CS	0.4	-0.2	0.2	-0.1	0.1	1.0	0.1	0.5	-0.0	0.3	0.2	0.3	-0.1	-0.0	0.7	0.1	0.4	0.4	0.2	-0.1	0.1	0.1	0.2	CS
CR	-0.1	-0.0	0.2	0.1	0.1	0.1	1.0	0.2	0.1	0.2	-0.1	0.1	0.0	0.2	0.2	-0.0	-0.0	0.0	0.4	0.0	0.6	0.1	-0.0	CR
CU	0.3	-0.2	0.3	-0.1	0.1	0.5	0.2	1.0	0.1	0.5	0.2	0.0	-0.0	-0.0	0.5	0.2	0.3	0.4	0.3	0.1	0.1	0.2	0.2	CU
F	-0.0	-0.0	-0.1	-0.2	-0.1	-0.0	0.1	0.1	1.0	0.2	-0.3	-0.1	-0.2	0.0	-0.0	0.5	-0.2	-0.2	0.1	0.1	0.1	-0.1	-0.0	F
GA	0.2	-0.0	0.4	-0.0	0.0	0.3	0.2	0.5	0.2	1.0	0.2	0.2	-0.0	-0.1	0.4	0.1	0.2	0.3	0.2	0.1	0.1	0.1	0.2	GA
GE	0.4	0.3	0.5	0.0	0.3	0.2	-0.1	0.2	-0.3	0.2	1.0	0.2	0.3	0.0	0.4	-0.2	0.6	0.7	-0.2	0.0	-0.1	0.3	0.2	GE
MG	0.1	0.1	0.1	0.0	0.1	0.3	0.1	0.0	-0.1	0.2	0.2	1.0	-0.1	-0.1	0.4	0.1	0.2	0.4	-0.0	-0.1	0.1	0.1	-0.0	MG
MN	-0.1	0.4	0.2	-0.1	0.2	-0.1	0.0	-0.0	-0.2	-0.0	0.3	-0.1	1.0	0.2	0.1	-0.2	0.1	0.1	-0.1	0.1	0.2	0.2	-0.0	MN
MO	-0.2	0.2	-0.1	-0.1	0.1	-0.0	0.2	-0.0	0.0	-0.1	0.0	-0.1	0.2	1.0	0.0	-0.2	0.0	-0.1	0.1	-0.0	0.3	0.2	0.2	MO
NI	0.3	0.0	0.3	-0.1	0.2	0.7	0.2	0.5	-0.0	0.4	0.4	0.4	0.1	0.0	1.0	0.1	0.5	0.6	0.1	-0.1	0.2	0.3	0.1	NI
P	0.3	-0.2	-0.1	0.0	-0.1	0.1	-0.0	0.2	0.5	0.1	-0.2	0.1	-0.2	-0.2	0.1	1.0	0.1	-0.1	-0.0	-0.1	-0.1	-0.1	0.0	P
PB	0.7	-0.1	0.4	-0.1	0.1	0.4	-0.0	0.3	-0.2	0.2	0.6	0.2	0.1	0.0	0.5	0.1	1.0	0.6	-0.0	-0.1	0.0	0.2	0.1	PB
SB	0.6	0.0	0.4	-0.0	0.2	0.4	0.0	0.4	-0.2	0.3	0.7	0.4	0.1	-0.1	0.6	-0.1	0.6	1.0	-0.0	-0.1	0.0	0.2	0.3	SB
SE	0.0	-0.1	0.0	-0.1	0.0	0.2	0.4	0.3	0.1	0.2	-0.2	-0.0	-0.1	0.1	0.1	-0.0	-0.0	-0.0	1.0	0.0	0.4	0.0	0.2	SE
SN	-0.1	0.1	0.1	0.1	0.0	-0.1	0.0	0.1	0.1	0.1	0.0	-0.1	0.1	-0.0	-0.1	-0.1	-0.1	-0.1	0.0	1.0	0.0	0.1	-0.1	SN
V	-0.1	-0.1	0.0	0.1	-0.0	0.1	0.6	0.1	0.1	0.1	-0.1	0.1	0.2	0.3	0.2	-0.1	0.0	0.0	0.4	0.0	1.0	0.0	0.1	V
ZN	0.0	0.3	0.2	-0.1	0.9	0.1	0.1	0.2	-0.1	0.1	0.3	0.1	0.2	0.2	0.3	-0.1	0.2	0.2	0.0	0.1	0.0	1.0	-0.0	ZN
ZR	0.3	-0.0	0.0	-0.1	-0.0	0.2	-0.0	0.2	-0.0	0.2	0.2	-0.0	-0.0	0.2	0.1	0.0	0.1	0.3	0.2	-0.1	0.1	-0.0	1.0	ZR
AL	-0.2	0.1	0.0	-0.1	0.0	0.1	0.2	0.3	0.4	0.3	-0.2	-0.1	0.0	0.1	0.1	0.2	-0.1	-0.1	0.3	0.1	0.3	0.0	-0.1	AL
CA	-0.2	0.1	-0.2	-0.1	0.3	-0.2	-0.1	-0.1	-0.1	-0.1	0.0	-0.2	0.5	0.2	-0.2	-0.1	-0.1	-0.1	-0.2	0.1	0.1	0.3	0.1	CA
CL	0.0	-0.2	-0.2	0.2	-0.3	0.0	0.1	-0.2	0.0	-0.2	-0.3	-0.0	-0.2	-0.2	-0.1	-0.0	-0.1	-0.2	0.0	-0.1	0.1	-0.2	-0.1	CL
FE	0.2	0.2	0.3	-0.3	0.0	0.2	0.0	0.1	-0.0	-0.0	0.4	-0.0	0.2	0.3	0.2	-0.2	0.3	0.2	0.1	0.0	0.2	0.0	0.2	FE
K	-0.0	-0.1	0.1	-0.0	-0.0	0.3	0.4	0.4	0.3	0.3	-0.1	0.1	0.0	0.0	0.4	0.2	0.0	0.0	0.3	-0.0	0.4	0.0	-0.1	K
MG	-0.2	-0.0	-0.1	0.1	-0.1	-0.1	0.0	0.1	0.0	0.1	-0.1	-0.1	0.3	0.3	-0.1	0.1	-0.1	-0.1	-0.1	0.1	0.1	-0.0	0.1	MG
NA	-0.3	0.3	-0.2	0.0	-0.1	-0.2	0.2	-0.1	-0.0	-0.2	-0.2	-0.1	0.0	-0.0	-0.2	-0.1	-0.3	-0.3	0.0	0.1	-0.0	-0.1	-0.0	NA
SI	-0.3	0.2	-0.1	-0.1	0.0	0.1	0.3	0.2	0.3	0.2	-0.2	-0.1	0.2	0.2	0.2	0.1	-0.2	-0.2	0.2	0.1	0.4	0.0	-0.1	SI
TI	-0.1	-0.1	0.1	-0.0	0.0	0.0	0.2	0.2	0.2	0.3	-0.2	-0.1	-0.1	-0.1	0.1	0.1	-0.1	-0.1	0.3	0.0	0.4	-0.0	-0.1	TI
ORG	-0.3	0.6	0.2	-0.2	0.2	-0.2	0.2	-0.1	0.0	-0.0	0.2	-0.1	0.4	0.5	-0.0	-0.3	-0.0	-0.0	0.1	0.0	0.1	0.2	-0.0	ORG
PYS	0.3	0.1	0.2	-0.3	-0.1	0.2	0.0	0.1	0.1	-0.0	0.3	0.0	0.1	0.4	0.2	-0.1	0.4	0.2	0.2	0.0	0.2	-0.0	0.2	PYS
SUS	-0.0	-0.1	0.1	-0.2	0.1	0.4	0.4	0.3	0.2	0.1	-0.1	-0.0	0.1	0.1	0.2	0.2	0.0	-0.0	0.1	0.0	0.2	0.1	0.2	SUS
TOS	0.0	0.4	0.2	-0.3	0.1	0.1	0.1	0.1	0.1	-0.0	0.3	-0.0	0.3	0.5	0.1	-0.2	0.2	0.1	0.2	0.0	0.2	0.1	0.1	TOS
SKRF	-0.0	0.5	0.3	-0.3	0.1	-0.0	0.2	-0.0	-0.0	-0.0	0.4	-0.1	0.3	0.5	0.1	-0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	SKRF
ADL	-0.0	0.7	0.2	-0.0	0.1	-0.1	-0.1	0.1	-0.2	0.1	0.4	0.0	0.3	-0.0	0.1	-0.1	-0.0	0.1	0.1	0.1	-0.2	0.1	0.0	ADL
MOIS	-0.0	0.7	0.3	0.0	0.3	-0.2	-0.0	-0.1	-0.3	0.0	0.4	0.1	0.5	0.1	0.1	-0.2	0.1	0.2	-0.2	0.2	-0.2	0.2	0.0	MOIS
VOL	-0.2	0.5	0.1	-0.0	0.1	-0.3	-0.2	-0.2	-0.2	-0.1	0.3	-0.1	0.3	0.2	-0.3	-0.1	-0.1	0.0	-0.4	0.1	-0.4	0.1	0.1	VOL
FIXC	0.2	-0.5	-0.1	0.2	-0.1	0.2	0.1	-0.0	0.0	0.0	-0.2	0.2	-0.5	-0.4	0.1	0.1	0.0	0.0	0.1	-0.2	0.1	-0.1	-0.1	FIXC
ASH	-0.2	0.2	-0.0	-0.4	0.1	0.1	0.2	0.2	0.3	0.2	-0.0	-0.1	0.4	0.4	0.2	0.0	0.1	-0.1	0.3	0.1	0.4	0.1	0.0	ASH
BTU	0.3	-0.6	0.0	0.3	-0.1	0.4	-0.2	0.1	-0.0	-0.1	0.0	0.2	-0.4	-0.3	0.2	0.3	0.1	0.1	-0.2	-0.1	-0.3	-0.1	-0.0	BTU
C	0.2	-0.3	0.1	0.4	-0.1	0.0	-0.2	-0.2	-0.2	-0.1	0.1	0.1	-0.3	-0.4	-0.0	-0.0	0.1	0.1	-0.2	-0.1	-0.2	-0.1	-0.1	C
H	0.1	-0.0	0.1	0.1	0.0	-0.1	-0.2	-0.1	-0.1	-0.2	0.1	0.1	-0.2	-0.2	-0.1	-0.0	0.1	0.1	-0.2	0.0	-0.1	-0.0	-0.1	H
N	0.2	-0.1	-0.0	0.2	-0.1	-0.0	-0.1	-0.2	-0.0	-0.1	-0.0	0.1	-0.2	-0.3	0.1	0.0	0.0	0.1	-0.2	-0.2	-0.0	-0.1	-0.1	N
S	-0.2	0.2	-0.2	-0.0	0.0	-0.2	0.0	-0.0	0.0	0.0	-0.2	-0.1	-0.0	-0.1	-0.2	0.2	-0.3	-0.2	-0.1	0.1	-0.2	-0.0	0.2	S
HTA	-0.2	0.2	-0.0	-0.3	0.1	0.1	0.2	0.3	0.2	0.1	-0.0	-0.2	0.4	0.4	0.1	-0.0	0.0	-0.1	0.3	0.1	0.3	0.1	0.0	HTA
LTA	-0.1	0.3	0.1	-0.4	0.1	0.1	0.2	0.3	0.2	0.2	0.1	-0.2	0.4	0.3	0.1	-0.0	0.0	-0.0	0.3	0.3	0.3	0.1	0.1	LTA
	AS	B	BE	BR	CO	CS	CR	CU	F	GA	GE	MG	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR	

Note: All values are rounded to one significant figure. Abbreviations are the same as those used in preceding tables.

OF ANALYTICAL DETERMINATIONS ON 101 COALS

	AL	CA	CL	FE	K	MG	NA	SI	TI	ORS	PYS	SUS	TOS	SXRF	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	O	HTA	LTA	
AS	-0,2	-0,2	0,0	0,2	-0,0	-0,2	-0,3	-0,3	-0,1	-0,3	0,3	-0,0	0,0	-0,0	-0,0	-0,0	-0,2	0,2	-0,2	0,3	0,2	0,1	0,2	-0,2	-0,2	-0,1	AS
B	0,1	0,1	-0,2	0,2	-0,1	-0,0	0,3	0,2	-0,1	0,6	0,1	-0,1	0,4	0,5	0,7	0,7	0,5	-0,5	0,2	-0,6	-0,3	-0,0	-0,1	0,2	0,2	0,3	B
BE	0,0	-0,2	-0,2	0,3	0,1	-0,1	-0,2	-0,1	0,1	0,2	0,2	0,1	0,2	0,3	0,2	0,3	0,1	-0,1	-0,0	0,0	0,1	0,1	-0,0	-0,2	-0,0	0,1	BE
BR	-0,1	-0,1	0,2	-0,3	-0,0	0,1	0,0	-0,1	-0,0	-0,2	-0,3	-0,2	-0,3	-0,3	-0,0	0,0	-0,0	0,2	-0,4	0,3	0,4	0,1	0,2	-0,0	-0,3	-0,4	BR
CD	0,0	0,3	-0,2	0,0	-0,0	-0,1	-0,1	0,0	0,0	0,2	-0,1	0,1	0,1	0,1	0,1	0,3	0,1	-0,1	0,1	-0,1	-0,1	0,0	-0,1	0,0	0,1	0,1	CD
CO	0,1	-0,2	0,0	0,2	0,3	-0,1	-0,2	0,1	0,0	-0,2	0,2	0,4	0,1	-0,0	-0,1	-0,2	-0,3	0,2	0,1	0,4	0,0	-0,1	-0,0	-0,2	0,1	0,1	CO
CR	0,2	-0,1	0,0	0,0	0,4	0,0	0,2	0,3	0,2	0,2	0,0	0,4	0,1	0,2	-0,1	-0,0	-0,2	0,1	0,2	-0,2	-0,2	-0,2	-0,1	0,0	0,2	0,2	CR
CU	0,3	-0,1	-0,2	0,1	0,4	0,1	-0,1	0,2	0,2	-0,1	0,1	0,3	0,1	-0,0	0,1	-0,1	-0,2	-0,0	0,2	0,1	-0,2	-0,1	-0,2	-0,0	0,3	0,3	CU
F	0,6	-0,1	0,0	-0,0	0,3	0,0	-0,0	0,3	0,2	0,0	0,1	0,2	0,1	-0,0	-0,2	-0,3	-0,2	0,0	0,3	-0,0	-0,2	-0,1	-0,0	0,0	0,2	0,2	F
GA	0,3	-0,1	-0,2	-0,0	0,3	0,1	-0,2	0,2	0,3	-0,0	-0,0	0,1	-0,0	-0,0	0,1	0,0	-0,1	0,0	0,2	-0,1	-0,1	-0,2	-0,1	0,0	0,1	0,2	GA
GE	-0,2	0,0	-0,3	0,4	-0,1	-0,1	-0,2	-0,2	-0,2	0,2	0,3	-0,1	0,3	0,4	0,4	0,4	0,3	-0,2	-0,0	0,0	0,1	0,1	-0,0	-0,2	-0,0	0,1	GE
HG	-0,1	-0,2	-0,0	-0,0	0,1	-0,1	-0,1	-0,1	-0,1	-0,1	0,0	-0,0	-0,0	-0,1	0,0	0,1	-0,1	0,2	-0,1	0,2	0,1	0,1	0,1	-0,1	-0,2	-0,2	HG
MN	0,0	0,5	-0,2	0,2	0,0	0,3	0,0	0,2	-0,1	0,4	0,1	0,1	0,3	0,3	0,3	0,5	0,3	-0,5	0,6	-0,4	-0,3	-0,2	-0,2	-0,0	0,0	0,4	MN
MO	0,1	0,2	-0,2	0,3	0,0	0,3	-0,0	0,2	-0,1	0,5	0,4	0,1	0,5	0,5	-0,0	0,1	0,2	-0,4	0,4	-0,3	-0,4	-0,2	-0,3	-0,1	0,4	0,3	MO
NI	0,1	-0,2	-0,1	0,2	0,4	-0,1	-0,2	0,2	0,1	-0,0	0,2	0,2	0,1	0,1	0,1	0,1	-0,3	0,1	0,2	0,2	-0,0	-0,1	0,1	-0,2	0,1	0,1	NI
P	0,2	-0,1	-0,0	-0,2	0,2	0,1	-0,1	0,1	0,1	-0,3	-0,1	0,2	-0,2	-0,3	-0,1	-0,2	-0,1	0,1	0,0	0,3	-0,0	-0,0	0,0	0,2	-0,0	-0,0	P
PB	-0,1	-0,1	-0,1	0,3	0,0	-0,1	-0,3	-0,2	-0,1	-0,0	0,4	0,0	0,2	0,2	-0,0	0,1	-0,1	0,0	0,1	0,1	0,1	0,1	0,0	-0,3	0,0	0,0	PB
SB	-0,1	-0,1	-0,2	0,2	0,0	-0,1	-0,2	-0,2	-0,1	-0,0	0,2	-0,0	0,1	0,1	0,1	0,2	-0,0	0,0	-0,1	0,1	0,1	0,1	0,1	-0,2	-0,1	-0,0	SB
SE	0,3	-0,2	0,0	0,1	0,3	-0,1	0,0	0,2	0,3	0,1	0,2	0,1	0,2	0,1	0,1	-0,2	-0,4	0,1	0,3	-0,2	-0,2	-0,2	-0,2	-0,1	0,3	0,3	SE
SN	0,1	0,1	-0,1	0,0	-0,0	0,1	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,2	0,1	-0,2	0,1	-0,1	-0,1	0,0	-0,2	0,1	0,1	0,3	SN
V	0,3	0,1	0,1	0,2	0,4	0,1	-0,0	0,4	0,4	0,1	0,2	0,2	0,2	0,1	-0,2	-0,2	-0,4	0,1	0,4	-0,3	-0,2	-0,1	-0,0	-0,2	0,3	0,3	V
ZN	0,0	0,3	-0,2	0,0	0,0	-0,0	-0,1	0,0	-0,0	0,2	-0,0	0,1	0,1	0,1	0,1	0,2	0,1	-0,1	0,1	-0,1	-0,1	-0,0	-0,1	-0,0	0,1	0,1	ZN
ZR	-0,1	0,1	-0,1	0,2	-0,1	0,1	-0,0	-0,1	-0,1	-0,0	0,2	0,2	0,1	0,1	0,0	0,0	0,1	-0,1	0,0	-0,0	-0,1	-0,1	-0,1	0,2	0,0	0,1	ZR
AL	1,0	-0,1	-0,2	-0,1	0,6	0,4	-0,1	0,8	0,8	-0,0	-0,1	0,2	-0,1	-0,2	0,1	-0,1	-0,2	-0,1	0,6	-0,4	-0,5	-0,4	-0,3	0,3	0,4	0,4	AL
CA	-0,1	1,0	-0,2	-0,2	-0,3	0,3	0,0	0,1	-0,1	0,1	-0,1	-0,0	-0,0	-0,0	0,1	0,2	0,3	-0,3	'0,2	-0,4	-0,1	-0,1	-0,2	0,1	0,2	0,2	CA
CL	-0,2	-0,2	1,0	-0,2	-0,0	-0,2	0,5	-0,2	-0,1	-0,3	-0,1	-0,1	-0,2	-0,2	-0,4	-0,2	-0,3	0,4	-0,2	0,4	0,4	0,1	0,5	-0,2	-0,2	-0,3	CL
FE	-0,1	-0,2	-0,2	1,0	0,1	-0,1	-0,1	0,0	-0,1	0,5	0,8	0,3	0,8	0,8	0,2	0,0	0,1	-0,2	0,3	-0,2	-0,3	-0,0	-0,2	-0,3	0,3	0,5	FE
K	0,6	-0,3	-0,0	0,1	1,0	0,2	-0,1	0,7	0,6	0,0	0,1	0,4	0,1	-0,0	-0,2	-0,2	-0,5	0,2	0,5	-0,2	-0,3	-0,3	0,0	-0,1	0,4	0,4	K
MG	0,4	0,3	-0,2	-0,1	0,2	1,0	-0,1	0,5	0,2	-0,1	-0,1	0,1	-0,1	-0,2	-0,0	0,2	0,2	-0,4	0,4	-0,2	-0,4	-0,4	-0,3	0,4	0,3	0,3	MG
NA	-0,1	0,0	0,5	-0,1	-0,1	-0,1	1,0	0,1	-0,1	0,1	-0,1	0,0	-0,0	0,1	0,2	0,1	0,2	-0,1	-0,0	-0,1	-0,1	0,1	0,1	0,2	0,0	-0,0	NA
SI	0,8	0,1	-0,2	0,0	0,7	0,5	0,1	1,0	0,7	0,1	-0,0	0,4	0,1	-0,0	0,1	-0,1	-0,2	-0,3	0,8	-0,6	-0,7	-0,5	-0,3	0,2	0,7	0,6	SI
TI	0,8	-0,1	-0,1	-0,1	0,6	0,2	-0,1	0,7	1,0	-0,2	-0,2	0,1	-0,2	-0,3	0,1	-0,2	-0,5	0,2	0,4	-0,4	-0,2	-0,3	-0,1	0,1	0,3	0,3	TI
ORS	-0,0	0,1	-0,3	0,5	0,0	-0,1	0,1	0,1	-0,2	1,0	0,5	0,1	0,8	0,9	0,4	0,3	0,4	-0,5	0,3	-0,6	-0,4	-0,1	-0,3	-0,2	0,3	0,4	ORS
PYS	-0,1	-0,1	-0,1	0,8	0,1	-0,1	-0,1	-0,0	-0,2	0,5	1,0	0,2	0,9	0,7	-0,0	-0,0	0,0	-0,3	0,4	-0,2	-0,3	-0,0	-0,1	-0,4	0,4	0,5	PYS
SUS	0,2	-0,0	-0,1	0,3	0,4	0,1	0,0	0,4	0,1	0,1	0,2	1,0	0,3	0,2	-0,0	-0,3	-0,1	-0,2	0,5	-0,4	-0,5	-0,4	-0,3	0,1	0,5	0,4	SUS
TOS	-0,1	-0,0	-0,2	0,8	0,1	-0,1	-0,0	0,1	-0,2	0,8	0,9	0,3	1,0	0,9	0,2	0,1	0,2	-0,4	0,5	-0,5	-0,5	-0,1	-0,3	-0,3	0,5	0,6	TOS
SXRF	-0,2	-0,0	-0,2	0,8	-0,0	-0,2	0,1	-0,0	-0,3	0,9	0,7	0,2	0,9	1,0	0,3	0,2	0,3	-0,4	0,3	-0,4	-0,4	0,0	-0,2	-0,3	0,3	0,5	SXRF
ADL	0,1	0,1	-0,4	0,2	-0,2	-0,0	0,2	0,1	0,1	0,4	-0,0	-0,0	0,2	0,3	1,0	0,9	0,5	-0,5	0,1	-0,4	-0,4	-0,1	-0,6	0,4	0,1	0,2	ADL
MOIS	-0,1	0,2	-0,2	0,0	-0,2	0,2	0,1	-0,1	-0,2	0,3	-0,0	-0,3	0,1	0,2	0,9	1,0	0,6	-0,5	0,0	-0,4	-0,1	-0,1	-0,1	0,2	-0,1	0,1	MOIS
VOL	-0,2	0,3	-0,3	0,1	-0,5	0,2	0,2	-0,2	-0,5	0,4	0,0	-0,1	0,2	0,3	0,5	0,6	1,0	-0,8	-0,1	-0,6	-0,3	0,0	-0,3	0,4	-0,0	0,0	VOL
FIXC	-0,1	-0,3	0,4	-0,2	0,2	-0,4	-0,1	-0,3	0,2	-0,5	-0,3	-0,2	-0,4	-0,4	-0,5	-0,5	-0,8	1,0	-0,5	0,7	0,7	0,3	0,5	-0,3	-0,5	-0,5	FIXC
ASH	0,6	0,2	-0,2	0,3	0,5	0,4	-0,0	0,8	0,4	0,3	0,4	0,5	0,5	0,3	0,1	0,0	-0,1	-0,5	1,0	-0,9	-0,8	-0,6	-0,4	0,0	0,9	0,9	ASH
BTU	-0,4	-0,4	0,4	-0,2	-0,2	-0,2	-0,1	-0,6	-0,4	-0,6	-0,2	-0,4	-0,5	-0,4	-0,4	-0,4	-0,4	0,7	-0,9	1,0	0,9	0,5	0,4	-0,4	-0,9	-0,7	BTU
C	-0,5	-0,1	0,4	-0,3	-0,3	-0,4	-0,1	-0,7	-0,2	-0,4	-0,3	-0,5	-0,5	-0,4	-0,4	-0,1	-0,3	0,7	-0,8	0,9	1,0	0,6	0,6	-0,5	-0,9	-0,8	C
H	-0,4	-0,1	0,1	-0,0	-0,3	-0,4	0,1	-0,5	-0,3	-0,1	-0,0	-0,4	-0,1	0,0	-0,1	-0,1	0,0	0,3	-0,6	0,5	0,6	1,0	0,6	-0,6	-0,6	-0,5	H
N	-0,3	-0,2	0,5	-0,2	0,0	-0,3	0,1	-0,3	-0,1	-0,3	-0,1	-0,3	-0,3	-0,2	-0,4	-0,1	-0,3	0,5	-0,4	0,4	0,6	0,6	1,0	-0,6	-0,5	-0,5	N
O	0,3	0,1	-0,2	-0,3	-0,1	0,4	0,2	0,2	0,1	-0,2	-0,4	0,1	-0,3	-0,3	0,4	0,2	0,4	-0,3	0,0	-0,4	-0,5	-0,6	-0,6	1,0	0,0	0,0	O
HTA	0,4	0,2	-0,2	0,3	0,4	0,3	0,0	0,7	0,3	0,3	0,4	0,5	0,5	0,3	0,1	-0,1	-0,0	-0,5	0,9	-0,9	-0,9	-0,6	-0,5	0,0	1,0	0,8	HTA
LTA	0,4	0,2	-0,3	0,5	0,4	0,3	-0,0	0,6	0,3	0,4	0,5	0,4	0,6	0,5	0,2	0,1	0,0	-0,5	0,9	-0,7	-0,8	-0,5	-0,5	0,0	0,8	1,0	LTA
	AL	CA	CL	FE	K	MG	NA	SI	TI	ORS	PYS	SUS	TOS	SXRF	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	O	HTA	LTA	

TABLE 8—LINEAR REGRESSION (LEAST SQUARES) CORRELATION COEFFICIENTS

	AS	B	BE	BR	CD	CO	CR	CU	F	GA	GE	HG	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR	
AS	1,0	-0,3	0,2	-0,1	0,0	0,4	-0,2	0,4	-0,0	0,2	0,4	0,0	-0,1	-0,3	0,4	0,4	0,7	0,6	-0,1	-0,1	-0,2	0,0	0,4	AS
B	-0,3	1,0	0,1	-0,2	0,3	-0,2	-0,1	-0,0	-0,1	0,1	0,2	0,0	0,4	0,1	-0,1	-0,3	-0,3	-0,1	-0,0	0,2	-0,1	0,2	-0,0	B
BE	0,2	0,1	1,0	0,0	0,2	0,2	0,1	0,5	-0,1	0,4	0,5	0,0	0,1	-0,1	0,2	0,0	0,4	0,4	0,0	0,1	-0,1	0,2	0,1	BE
BR	-0,1	-0,2	0,0	1,0	-0,1	0,0	0,2	-0,1	-0,1	0,0	0,1	0,0	-0,1	-0,1	0,0	0,1	-0,1	-0,1	-0,1	0,0	0,2	-0,1	-0,1	BR
CD	0,0	0,3	0,2	-0,1	1,0	0,1	0,0	0,1	-0,2	0,1	0,3	0,1	0,2	0,1	0,1	-0,1	0,1	0,2	0,0	0,0	-0,0	0,9	0,0	CD
CO	0,4	-0,2	0,2	0,0	0,1	1,0	-0,0	0,4	-0,2	0,3	0,3	0,3	-0,2	-0,1	0,7	0,0	0,5	0,5	-0,0	-0,2	-0,1	0,1	0,3	CO
CR	-0,2	-0,1	0,1	0,2	0,0	-0,0	1,0	0,1	0,0	0,1	-0,2	0,0	-0,0	0,2	0,1	-0,0	-0,1	-0,1	0,4	-0,0	0,5	0,1	-0,0	CR
CU	0,4	-0,0	0,5	-0,1	0,1	0,4	0,1	1,0	0,0	0,5	0,3	0,1	-0,1	-0,1	0,5	0,1	0,4	0,5	0,2	0,1	-0,0	0,2	0,3	CU
F	-0,0	-0,1	-0,1	-0,1	-0,2	-0,2	0,0	0,0	1,0	0,1	-0,4	-0,1	-0,2	0,1	-0,1	0,4	-0,2	-0,3	-0,1	0,1	0,0	-0,1	-0,0	F
GA	0,2	0,1	0,4	0,0	0,1	0,3	0,1	0,5	0,1	1,0	0,3	0,3	-0,0	-0,1	0,4	0,1	0,2	0,4	0,0	0,0	-0,1	0,1	0,2	GA
GE	0,4	0,2	0,5	0,1	0,3	0,3	-0,2	0,3	-0,4	0,3	1,0	0,1	0,3	-0,0	0,4	-0,2	0,5	0,6	-0,1	0,1	-0,1	0,2	0,3	GE
HG	0,0	0,0	0,0	0,0	0,1	0,3	0,0	0,1	-0,1	0,3	0,1	1,0	-0,1	-0,1	0,4	0,1	0,1	0,3	-0,1	-0,1	0,0	0,1	-0,0	HG
MN	-0,1	0,4	0,1	-0,1	0,2	-0,2	-0,0	-0,1	-0,2	-0,0	0,3	-0,1	1,0	0,0	-0,1	-0,3	-0,0	0,1	-0,0	0,1	0,2	0,2	-0,0	MN
MO	-0,3	0,1	-0,1	-0,1	0,1	-0,1	0,2	-0,1	0,1	-0,1	-0,0	-0,1	0,0	1,0	-0,1	-0,3	-0,1	-0,2	0,3	-0,0	0,4	0,2	0,1	MO
NI	0,4	-0,1	0,2	0,0	0,1	0,7	0,1	0,5	-0,1	0,4	0,4	0,4	-0,1	-0,1	1,0	0,1	0,4	0,6	0,1	-0,1	0,0	0,2	0,2	NI
P	0,4	-0,3	0,0	0,1	-0,1	0,0	-0,0	0,1	0,4	0,1	-0,2	0,1	-0,3	-0,3	0,1	1,0	0,1	-0,0	-0,0	-0,1	-0,1	-0,2	0,0	P
PB	0,7	-0,3	0,4	-0,1	0,1	0,5	-0,1	0,4	-0,2	0,2	0,5	0,1	-0,0	-0,1	0,4	0,1	1,0	0,6	-0,0	-0,1	-0,1	0,1	0,1	PB
SB	0,6	-0,1	0,4	-0,1	0,2	0,5	-0,1	0,5	-0,3	0,4	0,6	0,3	0,1	-0,2	0,6	-0,0	0,6	1,0	-0,0	-0,1	-0,1	0,2	0,4	SB
SE	-0,1	-0,0	0,0	-0,1	0,0	-0,0	0,4	0,2	-0,1	0,0	-0,1	-0,1	-0,0	0,3	0,1	-0,0	-0,0	-0,0	1,0	-0,0	0,3	0,1	0,3	SE
SN	-0,1	0,2	0,1	0,0	0,0	-0,2	-0,0	0,1	0,1	0,0	0,1	-0,1	0,1	-0,0	-0,1	-0,1	-0,1	-0,1	-0,0	1,0	0,0	0,1	-0,1	SN
V	-0,2	-0,1	-0,1	0,2	-0,0	-0,1	0,5	-0,0	0,0	-0,1	-0,1	0,0	0,2	0,4	0,0	-0,1	-0,1	-0,1	0,3	0,0	1,0	0,0	0,1	V
ZN	0,0	0,2	0,2	-0,1	0,9	0,1	0,1	0,2	-0,1	0,1	0,2	0,1	0,2	0,2	0,2	-0,2	0,1	0,2	0,1	0,1	0,0	1,0	-0,0	ZN
ZR	0,4	-0,0	0,1	-0,1	0,0	0,3	-0,0	0,3	-0,0	0,2	0,3	-0,0	-0,0	0,1	0,2	0,0	0,1	0,4	0,3	-0,1	0,1	-0,0	1,0	ZR
AL	-0,3	0,3	0,1	-0,0	0,0	-0,1	0,2	0,1	0,4	0,2	-0,2	-0,1	0,0	0,2	0,1	0,1	-0,1	-0,2	0,2	-0,0	0,3	0,0	-0,1	AL
CA	-0,1	0,3	-0,2	-0,1	0,4	-0,2	-0,1	-0,3	-0,1	-0,2	0,1	-0,2	0,6	0,2	-0,2	-0,3	-0,1	-0,1	-0,0	0,1	0,2	0,3	0,0	CA
CL	-0,0	-0,4	-0,3	0,2	-0,2	0,0	0,1	-0,3	0,0	-0,3	-0,4	-0,1	-0,3	-0,2	-0,2	0,1	-0,1	-0,2	-0,0	-0,0	0,0	-0,2	-0,1	CL
FE	0,2	0,0	0,2	-0,2	-0,1	0,1	-0,1	0,2	-0,1	-0,0	0,3	-0,2	0,1	0,3	-0,1	-0,2	0,3	0,2	0,1	0,1	0,1	-0,1	0,3	FE
K	-0,2	-0,1	0,1	0,1	-0,1	-0,1	0,3	0,2	0,2	0,2	-0,3	0,1	-0,2	-0,0	0,1	0,2	-0,1	-0,1	0,0	-0,2	0,3	-0,1	-0,1	K
MG	-0,2	0,1	-0,0	-0,0	-0,1	-0,2	0,2	-0,0	0,0	0,0	-0,1	-0,1	0,3	0,2	0,0	-0,0	-0,1	-0,1	-0,0	-0,0	0,5	-0,0	-0,0	MG
NA	-0,3	0,3	-0,2	0,0	-0,1	-0,2	0,3	-0,2	0,0	-0,1	-0,2	-0,2	0,0	-0,0	-0,3	-0,1	-0,4	-0,3	0,1	0,2	0,1	-0,1	-0,0	NA
SI	-0,5	0,4	-0,0	-0,0	-0,0	-0,3	0,3	-0,1	0,1	-0,0	-0,2	-0,2	0,2	0,2	-0,1	-0,2	-0,3	-0,3	0,1	0,0	0,5	-0,0	-0,1	SI
TI	-0,2	0,1	0,1	0,1	0,1	-0,1	0,2	0,1	0,1	0,2	-0,2	-0,1	0,0	0,0	0,2	0,1	-0,0	-0,1	0,1	-0,0	0,4	0,0	-0,1	TI
GRS	-0,4	0,6	0,1	-0,2	0,2	-0,4	0,1	-0,2	0,0	0,0	0,1	-0,2	0,3	0,5	-0,4	-0,3	-0,2	-0,1	0,2	0,1	0,0	0,1	0,0	GRS
PYS	0,2	-0,1	0,1	-0,3	-0,2	0,0	-0,2	0,1	-0,0	-0,1	0,2	-0,1	-0,1	0,4	-0,1	-0,2	0,3	0,2	0,2	0,1	0,0	-0,2	0,3	PYS
SUS	-0,1	-0,1	0,2	-0,1	0,0	0,1	0,4	0,1	0,1	0,1	-0,1	-0,0	0,0	0,1	-0,0	0,0	-0,1	-0,0	0,1	-0,0	0,3	-0,0	0,3	SUS
YBS	-0,1	0,2	0,1	-0,3	-0,0	-0,2	-0,0	-0,0	0,0	-0,0	0,2	-0,2	0,1	0,5	-0,3	-0,3	0,1	0,0	0,2	0,1	0,1	-0,0	0,2	YBS
SURF	-0,2	0,4	0,2	-0,2	0,1	-0,2	0,1	0,0	-0,0	0,0	0,3	-0,3	0,2	0,5	-0,3	-0,4	0,0	0,0	0,1	0,2	0,0	0,1	0,2	SURF
ADL	-0,0	0,7	0,2	-0,0	0,1	-0,1	-0,1	0,1	-0,2	0,1	0,4	0,0	0,3	-0,0	0,1	-0,1	-0,0	0,1	0,1	0,1	-0,2	0,1	0,0	ADL
MGIS	-0,0	0,7	0,2	0,0	0,3	-0,1	0,0	0,1	-0,3	0,1	0,4	0,1	0,4	-0,1	0,1	-0,1	0,0	0,2	0,0	0,2	-0,1	0,3	-0,0	MGIS
VBL	-0,1	0,6	0,3	-0,2	0,2	-0,3	-0,1	-0,0	-0,0	0,1	0,5	-0,1	0,3	0,1	-0,3	-0,2	-0,1	0,1	-0,0	0,2	-0,2	0,1	0,1	VBL
FINE	0,2	-0,7	-0,3	0,3	-0,2	0,4	-0,0	0,1	0,1	-0,1	-0,3	0,2	-0,5	-0,3	0,3	0,3	0,1	-0,0	-0,2	-0,2	-0,0	-0,1	-0,1	FINE
ASH	-0,3	0,3	0,0	-0,4	-0,0	-0,3	0,2	-0,1	0,1	0,1	-0,1	-0,2	0,5	0,4	-0,2	-0,2	-0,1	-0,1	0,3	0,0	0,4	0,0	0,1	ASH
STU	0,3	-0,6	0,0	0,3	-0,1	0,4	-0,2	0,1	-0,0	-0,1	0,0	0,2	-0,4	-0,3	0,2	0,3	0,1	0,1	-0,2	-0,1	-0,3	-0,1	-0,0	STU
C	0,3	-0,5	-0,1	0,3	-0,1	0,3	-0,3	0,1	-0,1	-0,1	0,1	0,1	-0,3	-0,3	0,2	0,3	0,2	0,1	-0,3	-0,1	-0,3	-0,0	-0,1	C
H	0,1	-0,1	0,1	0,1	0,0	0,0	-0,2	0,1	-0,0	-0,1	0,1	0,0	-0,2	-0,1	-0,1	0,1	0,1	0,1	-0,2	0,1	-0,2	-0,0	-0,1	H
N	0,2	-0,4	-0,2	0,1	-0,2	0,1	-0,2	-0,1	0,0	-0,0	-0,2	0,1	-0,3	-0,4	0,1	0,1	-0,1	0,0	-0,2	-0,1	-0,1	-0,2	0,0	N
S	-0,2	0,5	0,0	0,0	0,1	-0,1	0,3	-0,1	-0,0	0,1	-0,1	0,1	0,0	-0,1	0,1	-0,0	-0,3	-0,1	0,0	0,1	-0,1	0,1	-0,0	S
HTA	-0,3	0,3	0,1	-0,3	0,0	-0,2	0,2	-0,1	0,1	0,0	-0,1	-0,3	0,5	0,4	-0,1	-0,3	-0,1	-0,1	0,3	0,0	0,5	0,0	0,1	HTA
LTA	-0,2	0,3	0,1	-0,2	0,1	-0,2	0,1	0,1	-0,1	0,1	0,1	-0,3	0,4	0,4	-0,2	-0,3	-0,1	-0,1	0,3	0,3	0,4	0,1	0,2	LTA
	AS	B	BE	BR	CD	CO	CR	CU	F	GA	GE	HG	MN	MO	NI	P	PB	SB	SE	SN	V	ZN	ZR	

Note: All values are rounded to one significant figure. Abbreviations are the same as those used in preceding tables.

OF ANALYTICAL DETERMINATIONS ON 82 ILLINOIS BASIN COALS

	AL	CA	CL	FE	K	MG	NA	SI	TI	GRS	PYS	SUS	TOS	SXRF	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	S	HTA	LTA
AS	-0.3	-0.1	-0.0	0.2	-0.2	-0.2	-0.3	-0.5	-0.2	-0.4	0.2	-0.1	-0.1	-0.2	-0.0	-0.0	-0.1	0.2	-0.3	0.3	0.3	0.1	0.2	-0.2	-0.3	-0.2
B	0.3	0.3	-0.4	0.0	-0.1	0.1	0.3	0.4	0.1	0.6	-0.1	-0.1	0.2	0.4	0.7	0.7	0.6	-0.7	0.3	-0.6	-0.5	-0.1	-0.4	0.5	0.3	0.3
BE	0.1	-0.2	-0.3	0.2	0.1	-0.0	-0.2	-0.0	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.3	-0.3	0.0	0.0	-0.1	0.1	-0.2	0.0	0.1	0.1
BR	-0.0	-0.1	0.2	-0.2	0.1	-0.0	0.0	-0.0	0.1	-0.2	-0.3	-0.1	-0.3	-0.2	-0.0	0.0	-0.2	0.3	-0.4	0.3	0.3	0.1	0.1	0.0	-0.3	-0.2
CD	0.0	0.4	-0.2	-0.1	-0.1	-0.1	-0.1	-0.0	0.1	0.2	-0.2	0.0	-0.0	0.1	0.1	0.3	0.2	-0.2	-0.0	-0.1	-0.1	0.0	-0.2	0.1	0.0	0.1
CO	-0.1	-0.2	0.0	0.1	-0.1	-0.2	-0.2	-0.3	-0.1	-0.4	0.0	0.1	-0.2	-0.2	-0.1	-0.1	-0.3	0.4	-0.3	0.4	0.3	0.0	0.1	-0.1	-0.2	-0.2
CR	0.2	-0.1	0.1	-0.1	0.3	0.2	0.3	0.3	0.2	0.1	-0.2	0.4	-0.0	0.1	-0.1	0.0	-0.1	-0.0	0.2	-0.2	-0.3	-0.2	-0.2	0.3	0.2	0.1
CU	0.1	-0.3	-0.3	0.2	0.2	-0.0	-0.2	-0.1	0.1	-0.2	0.1	0.1	-0.0	0.0	0.1	0.1	-0.0	0.1	-0.1	0.1	0.1	0.1	-0.1	-0.1	-0.1	0.1
F	0.4	-0.1	0.0	-0.1	0.2	0.0	0.0	0.1	0.1	0.0	-0.0	0.1	0.0	-0.0	-0.2	-0.3	-0.2	0.1	0.1	-0.0	-0.1	-0.0	0.0	-0.0	0.1	-0.1
GA	0.2	-0.2	-0.3	-0.0	0.2	0.0	-0.1	-0.0	0.2	0.0	-0.1	0.1	-0.0	0.0	0.1	0.1	0.1	-0.1	0.1	-0.1	-0.1	-0.1	-0.0	0.1	0.0	0.1
GE	-0.2	0.1	-0.4	0.3	-0.3	-0.1	-0.2	-0.2	-0.2	0.1	0.2	-0.1	0.2	0.3	0.4	0.4	0.5	-0.3	-0.1	0.0	0.1	0.1	-0.2	-0.1	-0.1	0.1
HG	-0.1	-0.2	-0.1	-0.2	0.1	-0.1	-0.2	-0.2	-0.1	-0.2	-0.1	-0.0	-0.2	-0.3	0.0	0.1	-0.1	0.2	-0.2	0.2	0.1	0.0	0.1	0.1	-0.3	-0.3
MN	0.0	0.6	-0.3	0.1	-0.2	0.3	0.0	0.2	0.0	0.3	-0.1	0.0	0.1	0.2	0.3	0.4	0.3	-0.5	0.5	-0.4	-0.3	-0.2	-0.3	0.0	0.5	0.4
MO	0.2	0.2	-0.2	0.3	-0.0	0.2	-0.0	0.2	0.0	0.5	0.4	0.1	0.5	0.5	-0.0	-0.1	0.1	-0.3	0.4	-0.3	-0.3	-0.1	-0.4	-0.1	0.4	0.4
NI	0.1	-0.2	-0.2	-0.1	0.1	0.0	-0.3	-0.1	0.2	-0.4	-0.1	-0.0	-0.3	-0.3	0.1	0.1	-0.3	0.3	-0.2	0.2	0.2	-0.1	0.1	0.1	-0.1	-0.2
P	0.1	-0.3	0.1	-0.2	0.2	-0.0	-0.1	-0.2	0.1	-0.3	-0.2	0.0	-0.3	-0.4	-0.1	-0.1	-0.2	0.3	-0.2	0.3	0.3	0.1	0.1	-0.0	-0.3	-0.3
PB	-0.1	-0.1	-0.1	0.3	-0.1	-0.1	-0.4	-0.3	-0.0	-0.2	0.3	-0.1	0.1	0.0	-0.0	0.0	-0.1	0.1	-0.1	0.1	0.2	0.1	-0.1	-0.3	-0.1	-0.1
SB	0.2	-0.1	-0.2	0.2	-0.1	-0.1	-0.3	-0.3	-0.1	-0.1	0.2	-0.0	0.0	0.0	0.1	0.2	0.1	-0.0	-0.1	0.1	0.1	0.1	0.0	-0.1	-0.1	-0.1
SE	0.2	-0.0	-0.0	0.1	0.0	-0.0	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.0	-0.0	-0.2	0.3	-0.2	-0.3	-0.2	-0.2	0.0	0.3	0.3
SN	-0.0	0.1	-0.0	0.1	-0.2	-0.0	0.2	0.0	-0.0	0.1	0.1	-0.0	0.1	0.2	0.1	0.2	0.2	-0.2	0.0	-0.1	-0.1	0.1	-0.1	0.1	0.0	0.3
V	0.3	0.2	0.0	0.1	0.3	0.5	0.1	0.5	0.4	0.0	0.0	0.3	0.1	0.0	-0.2	-0.1	-0.2	-0.0	0.4	-0.3	-0.3	-0.2	-0.1	-0.1	0.5	0.4
ZN	0.0	0.3	-0.2	-0.1	-0.1	-0.0	-0.1	-0.0	0.0	0.1	-0.2	-0.0	-0.0	0.1	0.1	0.3	0.1	-0.1	0.0	-0.1	-0.0	-0.0	-0.2	0.1	0.0	0.1
ZR	-0.1	0.0	-0.1	0.3	-0.1	-0.0	-0.0	-0.1	-0.1	0.0	0.3	0.3	0.2	0.2	0.0	-0.0	0.1	-0.1	0.1	-0.0	-0.1	-0.1	0.0	-0.0	0.1	0.2
AL	1.0	-0.1	-0.2	-0.0	0.5	0.4	0.1	0.7	0.7	0.1	-0.2	0.0	-0.1	-0.1	0.1	0.1	-0.1	-0.1	0.3	-0.4	-0.3	-0.2	-0.1	0.3	0.4	0.2
CA	-0.1	1.0	-0.2	-0.1	-0.2	0.2	-0.0	0.1	-0.1	0.3	-0.0	-0.0	0.1	0.2	0.1	0.2	0.2	-0.3	0.4	-0.4	-0.2	-0.1	-0.2	-0.1	0.4	0.3
CL	-0.2	-0.2	1.0	-0.3	-0.0	-0.2	0.5	-0.2	-0.1	-0.5	-0.2	-0.1	-0.4	-0.4	-0.4	-0.3	-0.4	0.5	-0.3	0.4	0.4	0.1	0.5	-0.1	-0.3	-0.4
FE	-0.0	-0.1	-0.3	1.0	-0.3	0.1	-0.2	-0.0	0.0	0.3	0.7	0.2	0.7	0.7	0.2	-0.1	0.3	-0.4	0.3	-0.2	-0.4	0.0	-0.3	-0.1	0.4	0.5
K	0.5	-0.2	-0.0	-0.3	1.0	0.4	-0.0	0.6	0.7	-0.3	-0.4	0.2	-0.4	-0.4	-0.2	-0.2	-0.4	0.3	0.2	-0.2	-0.1	-0.2	0.1	0.2	0.3	0.0
MG	0.4	0.2	-0.2	0.1	0.4	1.0	-0.1	0.5	0.4	0.1	-0.1	0.2	0.0	0.0	-0.0	-0.1	-0.2	-0.0	0.4	-0.2	-0.3	-0.2	-0.1	0.0	0.4	0.3
NA	0.1	-0.0	0.5	-0.2	-0.0	-0.1	1.0	0.2	-0.0	0.2	-0.2	0.0	-0.0	0.1	0.2	0.2	0.2	-0.1	0.0	-0.1	-0.2	-0.1	0.0	0.3	0.1	0.0
SI	0.7	0.1	-0.2	-0.0	0.6	0.5	0.2	1.0	0.8	0.3	-0.3	0.2	-0.0	0.1	0.1	0.0	-0.0	-0.3	0.6	-0.6	-0.6	-0.4	-0.1	0.4	0.7	0.5
TI	0.7	-0.1	-0.1	0.0	0.7	0.4	-0.0	0.8	1.0	-0.1	-0.3	0.2	-0.2	-0.2	0.1	0.0	-0.3	0.1	0.3	-0.4	-0.3	-0.3	0.0	0.3	0.4	0.3
GRS	0.1	0.3	-0.5	0.3	-0.3	0.1	0.2	0.3	-0.1	1.0	0.3	0.1	0.8	0.8	0.4	0.2	0.7	-0.8	0.5	-0.6	-0.7	-0.2	-0.6	0.2	0.5	0.5
PYS	-0.2	-0.0	-0.2	0.7	-0.4	-0.1	-0.2	-0.3	-0.3	0.3	1.0	-0.0	0.8	0.6	-0.0	-0.2	0.2	-0.3	0.3	-0.2	-0.3	0.0	-0.3	-0.4	0.3	0.4
SUS	0.0	-0.0	-0.1	0.2	0.2	0.2	0.0	0.2	0.2	0.1	-0.0	1.0	0.2	0.1	-0.0	-0.3	-0.1	-0.1	0.4	-0.4	-0.4	-0.3	-0.2	0.2	0.4	0.3
TOS	-0.1	0.1	-0.4	0.7	-0.4	0.0	-0.0	-0.0	-0.2	0.8	0.8	0.2	1.0	0.9	0.2	-0.0	0.5	-0.7	0.5	-0.5	-0.6	-0.1	-0.5	-0.1	0.6	0.6
SXRF	-0.1	0.2	-0.4	0.7	-0.4	0.0	0.1	0.1	-0.2	0.8	0.6	0.1	0.9	1.0	0.3	0.1	0.6	-0.7	0.4	-0.4	-0.6	-0.0	-0.6	-0.0	0.5	0.6
ADL	0.1	0.1	-0.4	0.2	-0.2	-0.0	0.2	0.1	0.1	0.4	-0.0	-0.0	0.2	0.3	1.0	0.9	0.5	-0.5	0.1	-0.4	-0.4	-0.1	-0.4	0.4	0.1	0.2
MOIS	0.1	0.2	-0.3	-0.1	-0.2	-0.1	0.2	0.0	0.0	0.2	-0.2	-0.3	-0.0	0.1	0.9	1.0	0.5	-0.5	0.0	-0.4	-0.2	-0.0	-0.3	0.4	0.0	0.1
VOL	-0.1	0.2	-0.4	0.3	-0.4	-0.2	0.2	-0.0	-0.3	0.7	0.2	-0.1	0.5	0.6	0.5	0.5	1.0	-0.9	0.1	-0.4	-0.3	0.2	-0.3	0.1	0.1	0.2
FIXC	-0.1	-0.3	0.5	-0.4	0.3	-0.0	-0.1	-0.3	0.1	-0.8	-0.3	-0.1	-0.7	-0.7	-0.5	-0.5	-0.9	1.0	-0.6	0.7	0.7	0.1	0.5	-0.1	-0.6	-0.5
ASH	0.3	0.4	-0.3	0.3	0.2	0.4	0.0	0.6	0.3	0.5	0.3	0.4	0.5	0.4	0.1	0.0	0.1	-0.6	1.0	-0.9	-0.8	-0.5	-0.4	0.1	1.0	0.8
BTU	-0.4	-0.4	0.4	-0.2	-0.2	-0.2	-0.1	-0.6	-0.4	-0.6	-0.2	-0.4	-0.5	-0.4	-0.4	-0.4	-0.4	0.7	-0.9	1.0	0.9	0.5	0.4	-0.4	-0.9	-0.7
C	-0.3	-0.2	0.4	-0.4	-0.1	-0.3	-0.2	-0.6	-0.3	-0.7	-0.3	-0.4	-0.6	-0.6	-0.4	-0.2	-0.3	0.7	-0.8	0.9	1.0	0.5	0.5	-0.5	-0.8	-0.7
H	-0.2	-0.1	0.1	0.0	-0.2	-0.2	-0.1	-0.4	-0.3	-0.2	0.0	-0.3	-0.1	-0.0	-0.1	-0.0	0.2	0.1	-0.5	0.5	0.5	1.0	0.1	-0.4	-0.5	-0.4
N	-0.1	-0.2	0.5	-0.3	0.1	-0.1	0.0	-0.1	0.0	-0.6	-0.3	-0.2	-0.5	-0.6	-0.4	-0.3	-0.3	0.5	-0.4	0.4	0.5	0.1	1.0	-0.2	-0.4	-0.5
S	0.3	-0.1	-0.1	-0.1	0.2	0.0	0.3	0.4	0.3	0.2	-0.4	0.2	-0.1	-0.0	0.4	0.4	0.1	-0.1	0.1	-0.4	-0.5	-0.4	-0.2	1.0	0.1	0.1
HTA	0.4	0.4	-0.3	0.4	0.3	0.4	0.1	0.7	0.4	0.5	0.3	0.4	0.6	0.5	0.1	0.0	0.1	-0.6	1.0	-0.9	-0.8	-0.5	-0.4	0.1	1.0	0.8
LTA	0.2	0.3	-0.4	0.5	0.0	0.3	0.0	0.5	0.3	0.5	0.4	0.3	0.6	0.6	0.2	0.1	0.2	-0.5	0.8	-0.7	-0.7	-0.4	-0.5	0.1	0.8	1.0
	AL	CA	CL	FE	K	MG	NA	SI	TI	GRS	PYS	SUS	TOS	SXRF	ADL	MOIS	VOL	FIXC	ASH	BTU	C	H	N	S	HTA	LTA

Figures 1-39

In figures 1 through 39, the data from Illinois Basin coals are plotted as unpatterned bars, those from the western United States as horizontally striped bars, and those from the eastern United States as vertically striped bars.

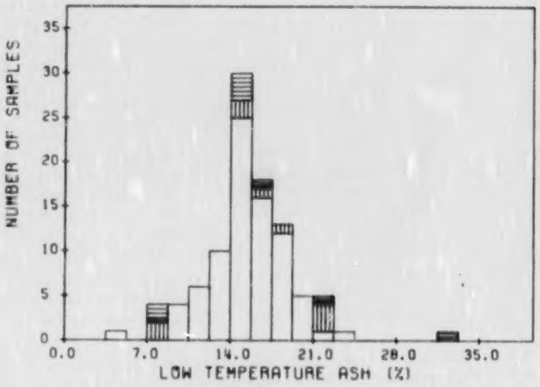

Fig. 1 - Distribution of low-temperature ash in coals analyzed.

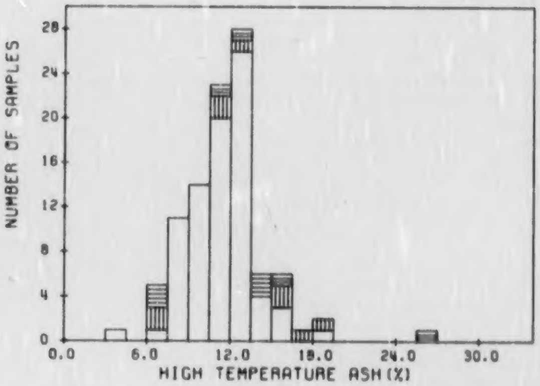

Fig. 2 - Distribution of high-temperature ash in coals analyzed.

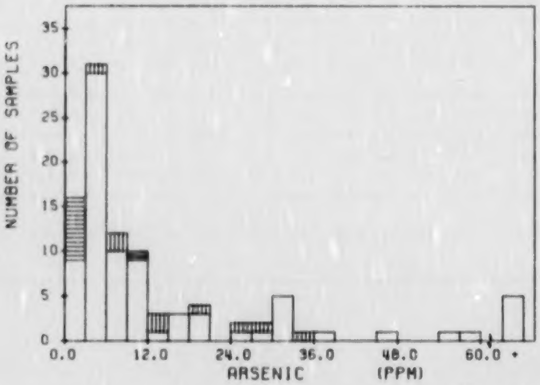

Fig. 3 - Distribution of arsenic in coals analyzed.

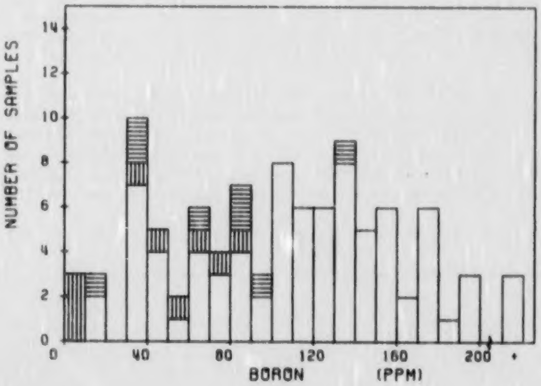

Fig. 4 - Distribution of boron in coals analyzed.

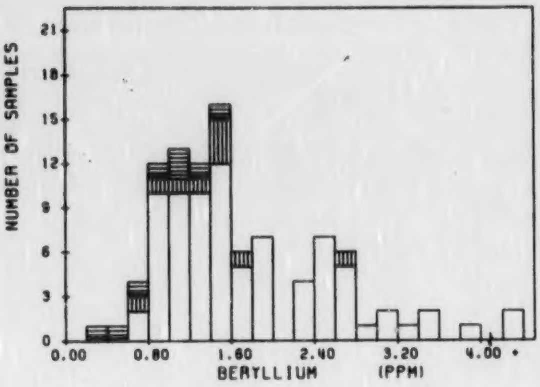

Fig. 5 - Distribution of beryllium in coals analyzed.

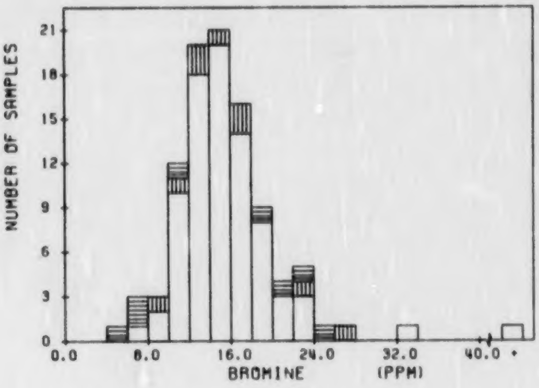

Fig. 6 - Distribution of bromine in coals analyzed.

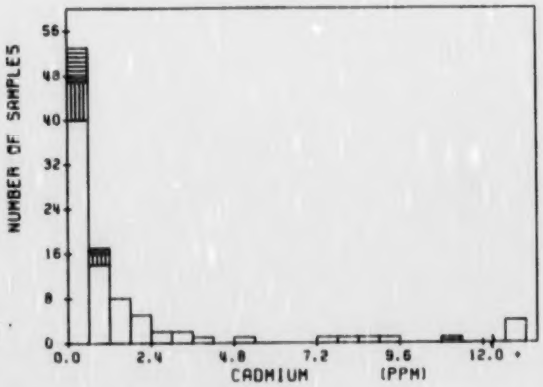

Fig. 7 - Distribution of cadmium in coals analyzed.

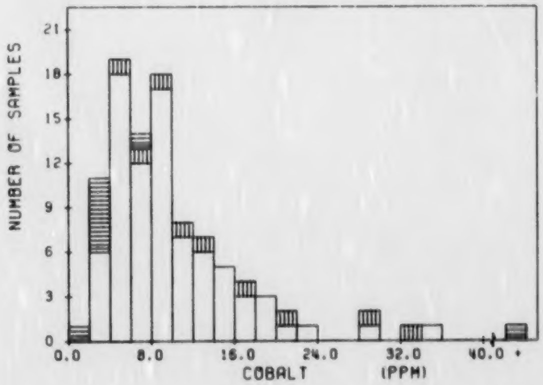

Fig. 8 - Distribution of cobalt in coals analyzed.

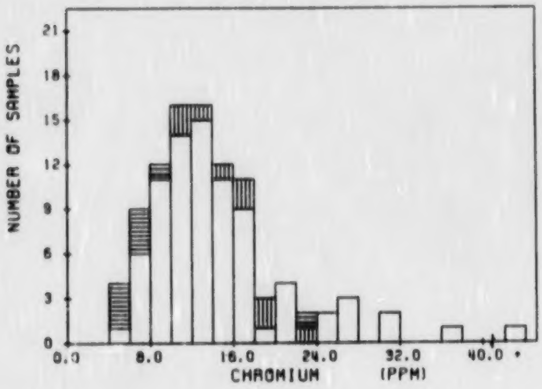

Fig. 9 - Distribution of chromium in coals analyzed.

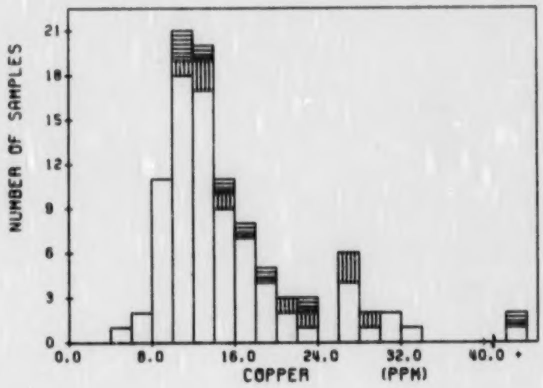

Fig. 10 - Distribution of copper in coals analyzed.

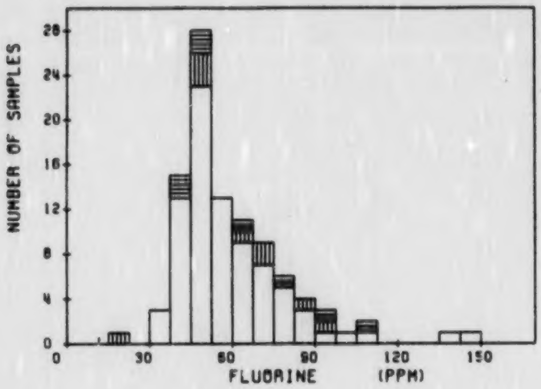

Fig. 11 - Distribution of fluorine in coals analyzed.

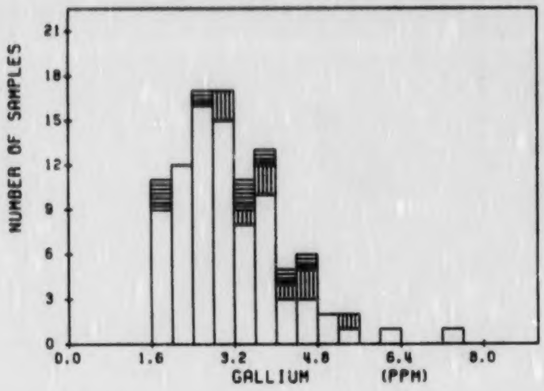

Fig. 12 - Distribution of gallium in coals analyzed.

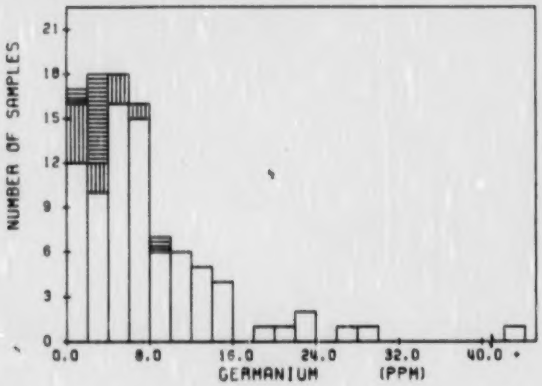

Fig. 13 - Distribution of germanium in coals analyzed.

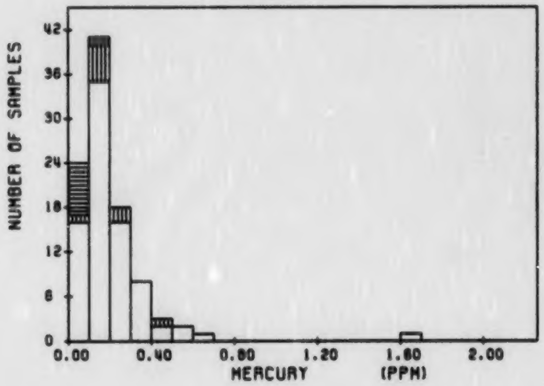

Fig. 14 - Distribution of mercury in coals analyzed.

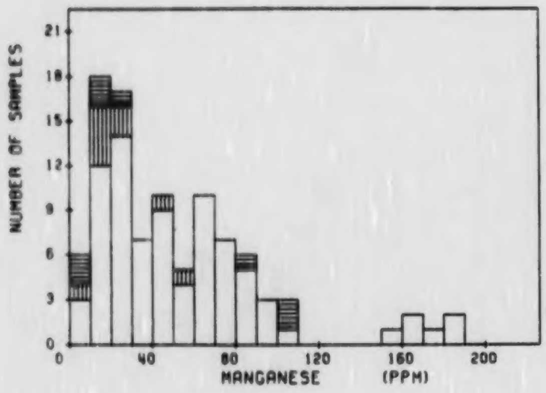

Fig. 15 - Distribution of manganese in coals analyzed.

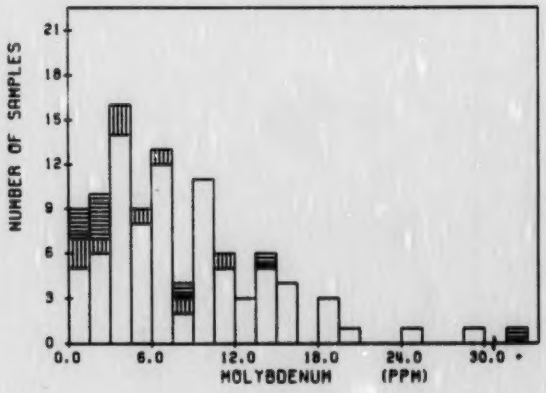

Fig. 16 - Distribution of molybdenum in coals analyzed.

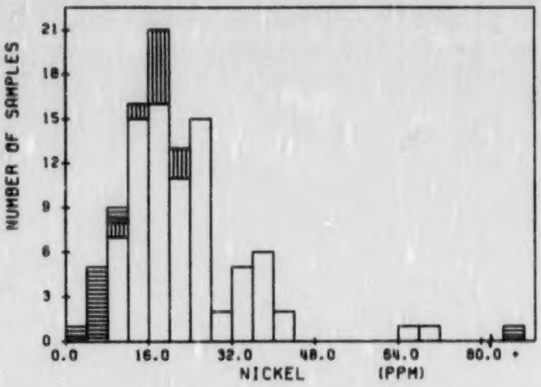

Fig. 17 - Distribution of nickel in coals analyzed.

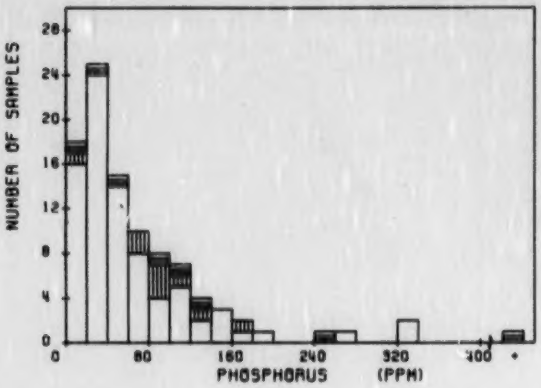

Fig. 18 - Distribution of phosphorus in coals analyzed.

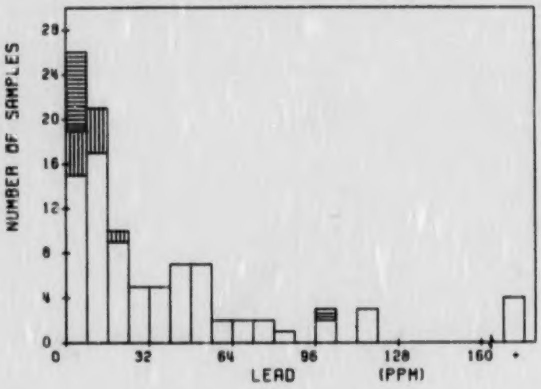

Fig. 19 - Distribution of lead in coals analyzed.

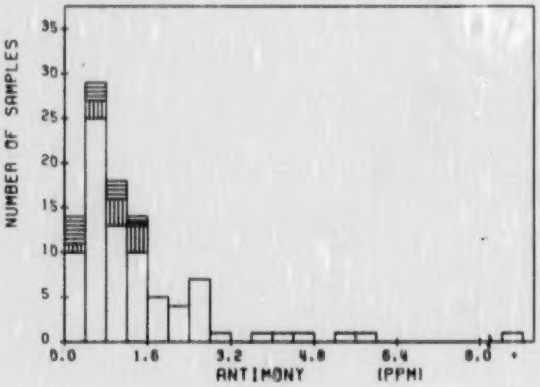

Fig. 20 - Distribution of antimony in coals analyzed.

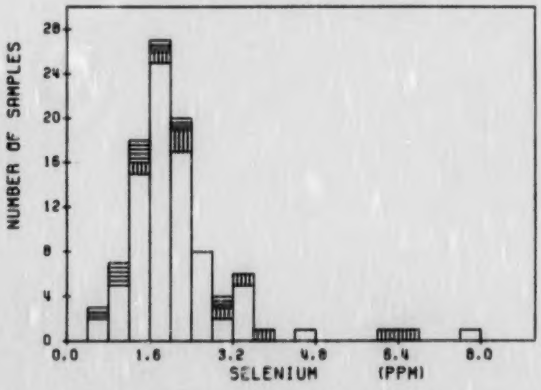

Fig. 21 - Distribution of selenium in coals analyzed.

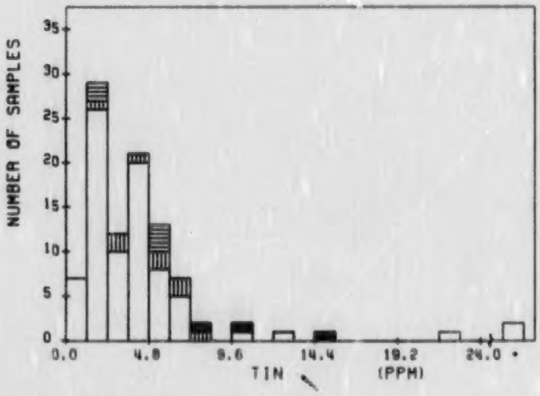

Fig. 22 - Distribution of tin in coals analyzed.

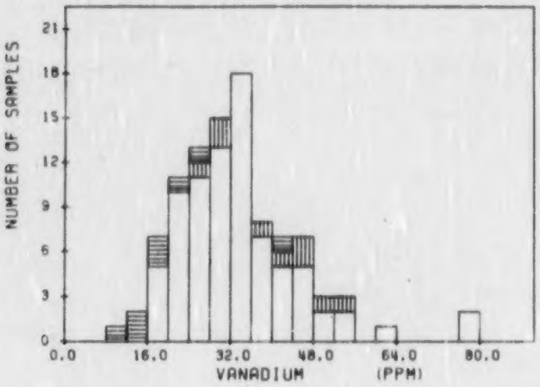

Fig. 23 - Distribution of vanadium in coals analyzed.

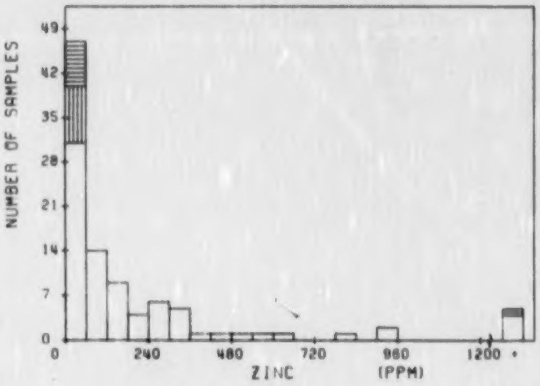

Fig. 24 - Distribution of zinc in coals analyzed.

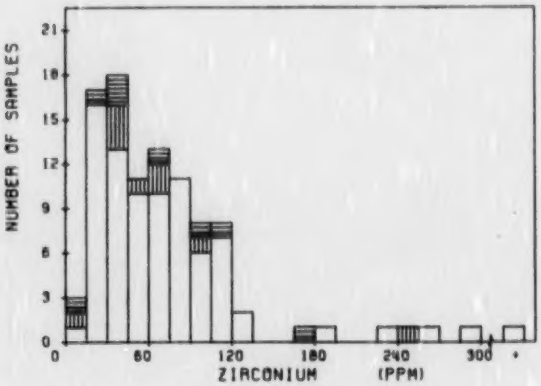

Fig. 25 - Distribution of zirconium in coals analyzed.

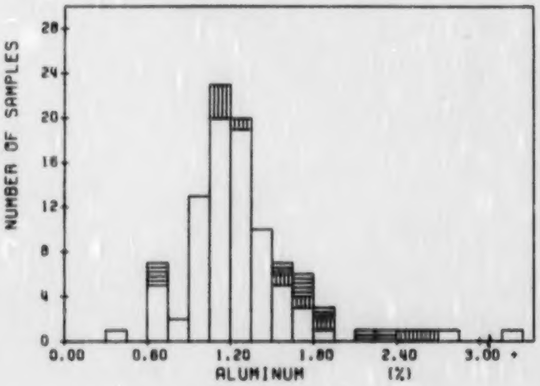

Fig. 26 - Distribution of aluminum in coals analyzed.

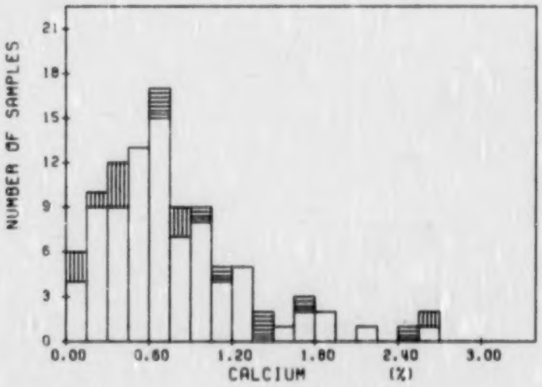

Fig. 27 - Distribution of calcium in coals analyzed.

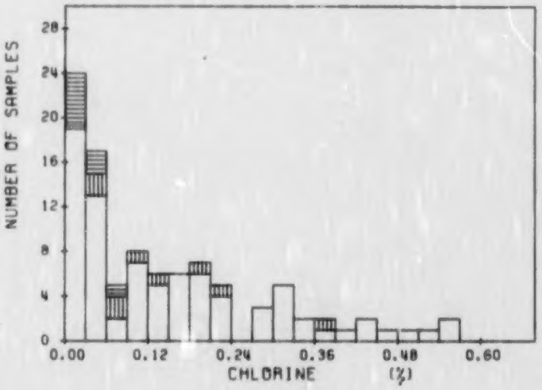

Fig. 28 - Distribution of chlorine in coals analyzed.

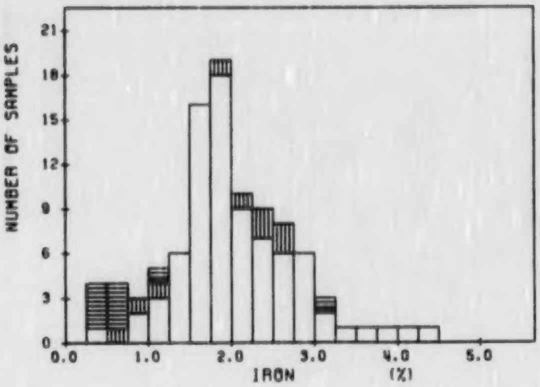

Fig. 29 - Distribution of iron in coals analyzed.

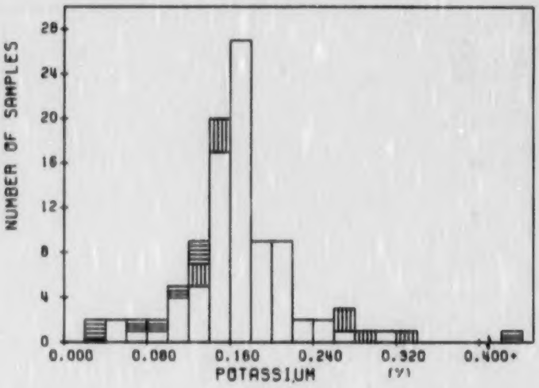

Fig. 30 - Distribution of potassium in coals analyzed.

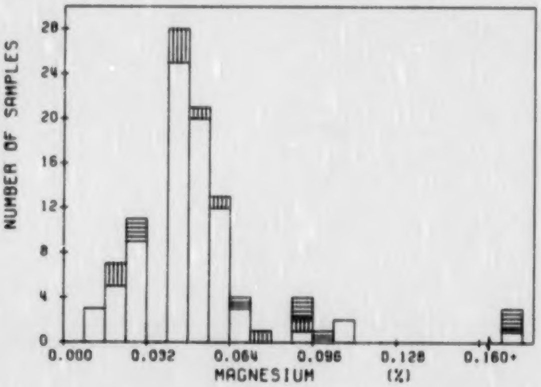

Fig. 31 - Distribution of magnesium in coals analyzed.

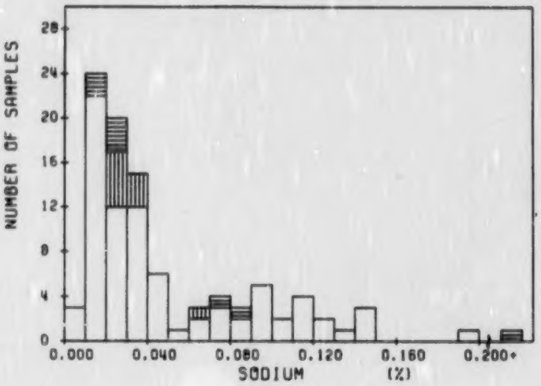

Fig. 32 - Distribution of sodium in coals analyzed.

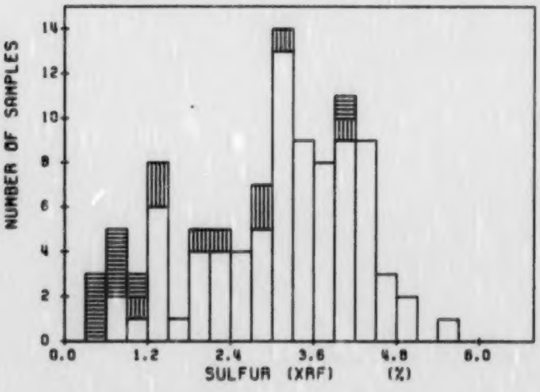

Fig. 33 - Distribution of sulfur in coals analyzed; determined by X-ray fluorescence.

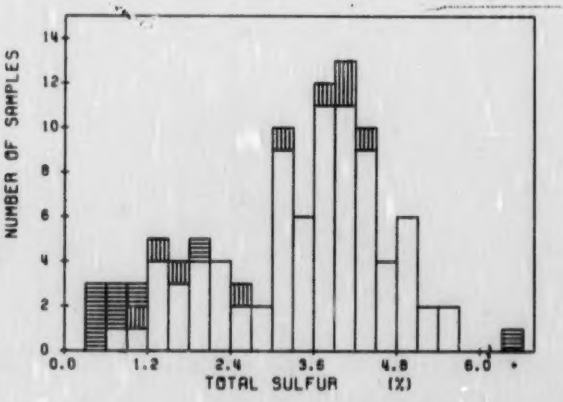

Fig. 34 - Distribution of sulfur in coals analyzed; determined by ASTM method.

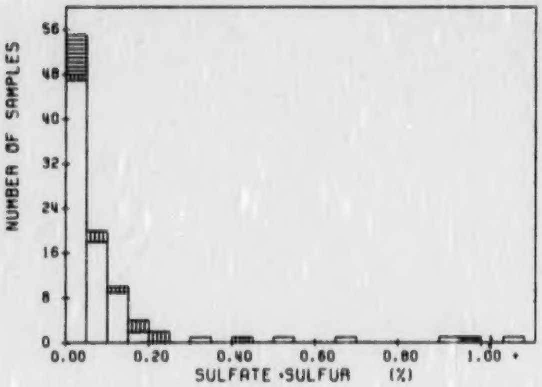

Fig. 35 - Distribution of sulfate sulfur in coals analyzed.

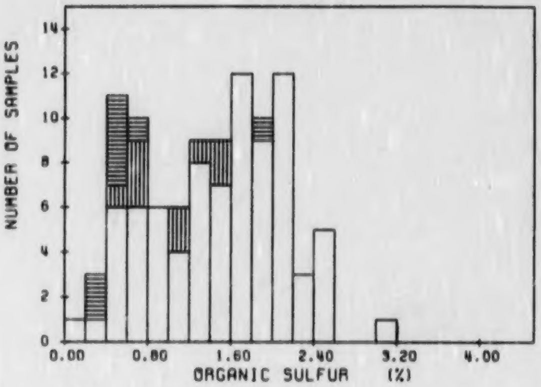

Fig. 36 - Distribution of organic sulfur in coals analyzed.

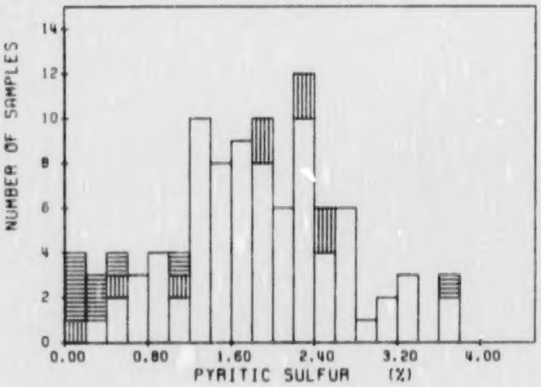

Fig. 37 - Distribution of pyritic sulfur in coals analyzed.

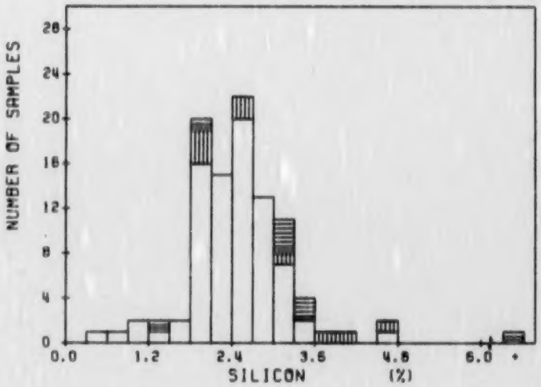

Fig. 38 - Distribution of silicon in coals analyzed.

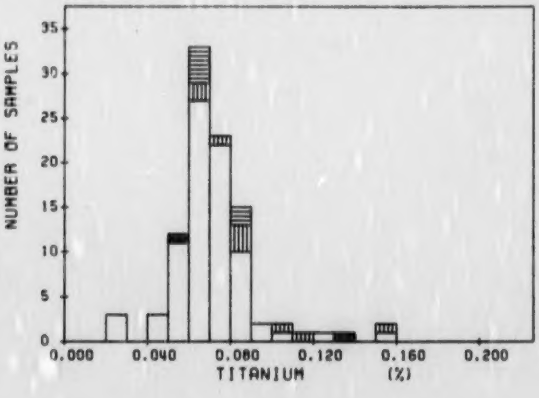

Fig. 39 - Distribution of titanium in coals analyzed.

3) There are mutually positive correlations between K, Ti, Al, and Si in the data reported here. These four elements are commonly found in nature as silicates, and are generally classified as lithophile elements. They occur in coals in the clay minerals and in quartz (plate 1, B, p. 53).

4) There is a positive correlation of 0.63 between Mn and Ca in coals of the Illinois Basin; Mn does not correlate as well with any other element. Manganese commonly substitutes for Ca in calcite ($CaCO_3$) and is probably in that combination in the coals (pl. 1, A).

5) Sodium and Cl have a positive correlation of 0.53 in both the Illinois Basin samples and all 101 samples. A similar correlation between chlorine and total alkalies was reported by Gluskoter and Rees (1964) and, in part, it can be attributed to Na and Cl having been deposited in coals from saline ground water (Gluskoter, 1965a; Gluskoter and Ruch, 1971).

The 82 coal samples of the Illinois Basin were further subdivided into four stratigraphic groups: coals below the Harrisburg-Springfield (No. 5) Coal Member, the Harrisburg-Springfield (No. 5) Coal Member, the Herrin (No. 6) Coal Member, and the coals above the Herrin (No. 6) Coal Member. Means, standard deviations, and correlation coefficients were determined for these four groups. Although the statistical data are not presented in this paper, the following relationships have been suggested from the statistics:

1) The concentrations of As, Cu, Pb, Si, and Al are lower in the younger coals than in the older coals of the Basin.

2) Boron may act as an indicator of paleosalinity (Bohor and Gluskoter, 1973). The concentration of boron in coal increases upward in the stratigraphic section, which suggests that the Illinois Basin became generally more saline during the period of time between deposition of the older and the younger coals.

3) The correlation between Na and Cl increased from the older coals to the younger coals, which is possibly a result of the basin becoming more saline.

Additional relationships have been suggested by the statistical analyses, and much more detailed statistical analyses and geochemical interpretations are underway, as is the mapping of the areal distribution of the elements within the Illinois Basin.

ENRICHMENT AND DEPLETION OF ELEMENTS IN COAL

Several geochemists have attempted to determine the abundance of chemical elements in the earth's crust; Clarke and Washington (1924) were among the first to do so. The term "clarke" is defined as the average percentage of an element in the earth's crust. The clarke values used in this report are taken from Taylor (1964).

A comparison of the concentration of an element in coal with the clarke value for that element provides an approximation as to the amount by which the element is enriched or depleted by the total coal-forming processes.

The 101 coal samples analyzed were divided into three groups: Illinois Basin coals, eastern United States coals, and western United States coals. (The Mississippi River was arbitrarily taken to be the line dividing eastern and western coals.)

Mean values were computed for the various trace elements in each group and the resulting means were divided by their clarke value. The resulting number is called an enrichment factor. Those elements whose enrichment factors are an order of magnitude greater or less than their clarke values (present in an amount greater than 10 times the clarke or less than one-tenth the clarke) are found in table 9. All other trace elements are present in amounts that approximate their abundance in the earth's crust (i.e., have the same order of magnitude).

The most significant aspect of table 9 is its brevity; only six of the elements analyzed were concentrated or depleted in coal by one order of magnitude or more. Only three elements were found to be enriched to that degree. Cadmium is enriched in coals from the Illinois Basin but not in the other coals studied. Cadmium occurs in Illinois coals in solid solution with Zn in the mineral sphalerite (Gluskoter and Lindahl, 1973). Sphalerite is not distributed uniformly within the Basin, but rather is concentrated in northwestern and southeastern Illinois. It occurs as epigenetic cleat (vertical fracture) filling.

TABLE 9—ENRICHMENT FACTORS OF CHEMICAL ELEMENTS IN COAL
(only those enriched or depleted by one order of magnitude or more are listed)

	Element	Enrichment factor	Mean value in coal	Clarke
Illinois Basin (81 samples)	B	11.38	113.79 ppm	10.0 ppm
	Cd	14.4	2.89 ppm	0.2 ppm
	F	0.09	59.30 ppm	625.0 ppm
	Mn	0.06	53.16 ppm	950.0 ppm
	P	0.06	62.77 ppm	1050.0 ppm
	Se	39.80	1.99 ppm	0.05 ppm
Eastern United States (9 samples)	F	0.10	62.5 ppm	625.0 ppm
	Mn	0.03	28.5 ppm	950.0 ppm
	P	0.09	94.5 ppm	1050.0 ppm
	Se	67.33	3.37 ppm	0.05 ppm
Western United States (8 samples)	Cr	0.09	9.0 ppm	100.0 ppm
	Mn	0.04	38.0 ppm	950.0 ppm
	Se	31.31	1.57 ppm	0.05 ppm

Boron is also concentrated in the coals of the Illinois Basin and not in the coals of eastern and western United States. A number of workers have used the B concentration in sediments and sedimentary rocks as an indicator of paleosalinity of the environment in which the sediment was originally deposited. An investigation of the B in the clay mineral illite in the low-temperature ash of Illinois coals has recently been reported (Bohor and Gluskoter, 1973). Greatly oversimplified, the use of the technique assumes that the relative concentrations of B in sediments and sedimentary rocks are directly dependent on the salinity of the water in which the sediments were deposited and that therefore marine sediments contain more B than non-marine sediments. However, the interpretation of B paleosalinity from even a carefully controlled set of samples is difficult. The set of samples reported upon here was not specifically collected for boron analyses or specially treated. The most obvious interpretation to be made from the observation that B is concentrated in the coals of the Illinois Basin and not in the coals from eastern and western United States is that the Illinois Basin coals were deposited in waters that had a higher salinity (more brackish or more marine) than did the waters in which the other coals were deposited. This interpretation, in general, does agree with the geologic interpretation of environments of deposition of the various coals based on other criteria. The coals of the Illinois Basin are generally more closely associated with marine strata than are the coals in the Appalachians or in the Rocky Mountain areas.

The third element that is found to be enriched in the coals is selenium, and it is concentrated to a significant degree in all three groups of coals. Selenium in the four laboratory-prepared coals (washed coals), discussed later, is interpreted to be in both organic and inorganic combination. We would suggest that organically combined Se may be inherited directly from Se concentrated by the plants in the original coal swamp. Further investigation of the distribution and mode of occurrence of Se in coals would be necessary to substantiate or refute this hypothesis.

RESULTS OF ANALYSES OF WASHED COALS

Many of the coals mined in the United States are "washed" or "cleaned" prior to delivery to the consumer. Cleaning involves reducing the ash and sulfur contents of the coal by removing a portion of the mineral matter associated with the coal. Because the specific gravities of the minerals in coal are from two to four times greater than that of the coal, most coal-cleaning techniques involve a specific gravity separation. Data on the washability of Illinois coals, as well as a description of the techniques used, have been published by Helfinstine et al. (1971, 1974) and Helfinstine et al. (1970).

Four samples of Illinois coals were separated into specific gravity fractions and analyzed for most of the same major, minor, and trace elements as were the 101 whole coals. The gravity separations were, in each case, made on a 3/8 inch by 28 mesh size fraction obtained by crushing the coal to less than 3/8 of an inch and then screening it. All separations of 1.60 specific gravity and below were made in an appropriate mixture of perchloroethylene and naphtha. The separations at a specific gravity of approximately 2.8 were made

TABLE 10—TRACE ELEMENTS
(parts per million,

SAMPLE NO.	SPECIFIC GRAVITY FRACTION*	PERCENT OF RAW COAL	COAL SEAM	AS	B	BE	CD	CO	CR	CU	GA	GE	HG
C-18090	3/8X28M	100,00	DV	8,7	22	3,0	1.7	3	10	11	1,4	8	0,24
C-18094	1,28F	25,87	DV	0,7	29	2,8	0,1	2	7	4	1,1	9	0,06
C-18095	1,30FS	19,50	DV	1,1	35	3,0	0,2	3	9	6	3,3	10	0,05
C-18096	1,32FS	19,70	DV	1,5	32	3,1	0,2	4	10	7	3,3	7	0,08
C-18097	1,40FS	19,30	DV	4,1	31	2,8	0,4	5	13	12	4,5	4	0,15
C-18098	1,60FS	7,20	DV	12,0	27	2,6	0,5	3	23	17	3,8	3	0,24
C-18099	>1,60	4,50	DV	61,0	4	1,8	20,0	8	21	18	1,7	4	2,10
C-18106	2,89FS	3,75	DV	34,0	36	3,7	2,4	10	27	23	4,9	5	0,70
C-18107	>2,90	4,75	DV	80,0	3	4,7	36,0	22	70	15	2,2	1	2,90
C-18092	3/8X28M	100,00	DK	15,0	24	4,8	0,6	6	15	11	3,0	6	0,62
C-18100	1,29F	19,40	DK	2,9	35	7,0	0,1	12	15	7	3,7	10	0,07
C-18105	1,60S	9,00	DK	181,0		7,1	2,4	19	44	17	3.1	6	4,00
C-18134	28MX0	100,00	2	83,0	90	3,2	20,0	8	10	34	2,2	30	0,24
C-18133	3/8X28M	100,00	2	113,0		4,5	47,0	10	18	35	2,1	35	0,24
C-18135	1,25F	28,20	2	14,0	70	2,6	0,1	5	4	13	2,3	30	0,08
C-18136	1,26FS	23,60	2	22,0	100	3,2	0,2	6	4	17	2,4	31	0,12
C-18137	1,30FS	27,60	2	47,0	170	3,2	0,4	8	5	20	0,8	23	0,21
C-18138	1,40FS	10,60	2	99,0	102	3,4	1,2	16	12	38	1,4	21	0,35
C-18139	1,60FS	3,20	2	175,0	96	3,1	11,0	15	18	69	4,1	14	0,38
C-18140	>1,60	6,80	2	630,0	42	7,0	338,0	18	140	140	13,0	10	1,20
C-18141	2,89FS	3,60	2	350,0	58	3,3	89,0	14	81	111	2,8	8	1,60
C-18142	>2,90	3.20	2	1109,0		5,2	710,0	12	42	177	1,3	8	9,40
C-18122	28MX0	100,00	6	11,0	137	2,5	3,2	5	25	25	4,8	13	0,17
C-18121	3/8X28M	100,00	6	15,0	96	2,2	6,1	5	32	23	4,7	9	0,18
C-18123	1,29F	36,10	6	0,9	90	2,3	0,2	2	8	5	2,1	15	0,07
C-18124	1,29FS	17,40	6	1,4	120	3,0	0,2	3	12	7	0,7	17	0,06
C-18125	1,33FS	14,70	6	2,3	190	3,0	0,2	5	16	10	2,6	13	0,09
C-18126	1,40FS	9,30	6	4,3	88	3,2	0,4	6	25	16	3,2	10	0,13
C-18127	1,60FS	6,90	6	5,8	73	3,1	0,7	5	33	25	5,2	6	0,17
C-18128	>1,60	15,60	6	58,0	80	3,2	27,0	19	71	65	12,0	1	0,68
C-18129	2,89FS	12,73	6	23,0	88	1,6	4,8	20	59	61	15,0	1	0,77
C-18130	>2,90	2,87	6	244,0		4,7	152,0	29	31	89	2,5	1	3,80

* Specific gravity fractions given followed by the letters FS indicate that the entire sample would float at that gravity and would sink at the gravity listed immediately above.

IN LABORATORY-PREPARED COALS
moisture-free coal)

SAMPLE NO.	SPECIFIC GRAVITY FRACTION*	PERCENT OF RAW COAL	COAL SEAM	MN	MO	NI	P	PB	SB	SE	V	ZN	ZR
C-18090	3/8X28M	100,00	OV	20	9	19	7	131	0,5	2,4	20	266	4
C-18094	1,28F	25,87	OV	8	2	9	13	12	0,3	1,6	13	31	1
C-18095	1,30FS	19,50	OV	8	1	14	17	17	0,3	1,7	13	37	2
C-18096	1,32FS	19,70	OV	10	1	16	24	19	0,4	1,6	18	41	4
C-18097	1,40FS	19,30	OV	15	3	20	30	40	0,5	2,1	35	56	4
C-18098	1,60FS	7,20	OV	34	10	19	22	101	0,9	3,2	90	121	12
C-18099	>1,60	8,50	OV	81	61	46	25	986	1,0	6,4	26	2525	18
C-18106	2,89FS	3,75	OV		24	33		392	3,6	5,4	29	487	18
C-18107	>2.90	4,75	OV	55	221	44		1465	1.2	7,2	78	4992	17
C-18092	3/8X28M	100,00	OK	13	12	17	85	125	0,5	1,5	26	120	6
C-18100	1,29F	19,40	OK	8	3	18	81	15	0,6	2,1	3	54	2
C-18105	1,60S	9,00	OK	26	135	38	167	880	0,8	5,8	58	429	19
C-18134	28MX0	100,00	2	65	12	30	23	183	3,4	1,1	20	1905	4
C-18133	3/8X28M	100,00	2	26	14	40	28	237	4,5	1,4	17	4772	2
C-18135	1,25F	28,20	2	5	2	16	21	81	3,9	0,8	8	13	1
C-18136	1,26FS	23,60	2	6	4	20	25	119	6,0	0,9	9	11	2
C-18137	1,30FS	27,60	2	8	8	26	21	205	3,5	1,2	11	23	3
C-18138	1,40FS	10,60	2	12	15	47	24	321	14,0	2,1	32	115	6
C-18139	1,60FS	3,20	2	24	20	60	21	448	16,0	3,1	36	665	9
C-18140	>1,60	6,80	2	209	111	116	14	753	11,0	3,5	46	32140	14
C-18141	2,89FS	3,60	2		34	98		633	18,0	3,7	52	7759	14
C-18142	>2,90	3,20	2	65	145	118		905	13,0	3,1	44	70160	20
C-18122	28MX0	100,00	6	130	13	29	64	100	1,9	3,7	39	313	10
C-18121	3/8X28M	100,00	6	89	11	38	39	135	1,9	3,4	32	603	12
C-18123	1,25F	36,10	6	7	5	9		13	1,2	1,1	16	7	1
C-18124	1,29FS	17,40	6	8	7	10	12	14	1,1	1,2	20	9	2
C-18125	1,33FS	14,70	6	10	8	15	15	25	1,3	1,8	26	12	4
C-18126	1,40FS	9,30	6	18	9	21	19	42	1,6	2,8	34	15	7
C-18127	1,60FS	6,90	6	34	12	25	24	58	1,6	3,5	38	41	8
C-18128	>1,60	15,60	6	365	28	77	100	530	4,2	8,8	72	3128	32
C-18129	2,89FS	12,73	6	457	14	76		210	2,8	6,8	60	570	
C-18130	>2,90	2.87	6	74	215	102		2162	12.0	21.0	85	15170	21

in bromoform or in bromoform which contained a small amount of ethyl alcohol. Three of the coals were each separated into six specific gravity fractions in the perchloroethylene and naphtha and the heaviest of each of these fractions (1.60 sink) was separated into two parts in bromoform. The fourth coal was also separated in the perchloroethylene and naphtha but only two fractions were analyzed, one with specific gravity of less than 1.25 and one with specific gravity greater than 1.60. The results of the analyses for Cl and Br in the washed coals are not given, since relatively large amounts of these elements were added to the coals from the washing media.

Results of the trace element determinations of the laboratory-prepared coals are given in table 10; the major and minor elements in table 11; the standard coal analyses in table 12; and varieties of sulfur in table 13. Samples are listed in order of increasing specific gravity. Those samples identified as to their size distribution (e.g., 3/8 in. by 28 mesh) are "whole coal," or the sample prior to washing.

The float-sink (washability) data may be displayed as washability curves and as histograms. Figures 40 through 71 are sets of such diagrams which are intended to show the "typical" distribution of each element in the four washed coal samples. There is a single set for each element determined, and the set may come from any one of the coals analyzed. A washability curve for the amount of low-temperature ash (LTA) in each of the three coals for which complete sets of washed samples were analyzed is also given for reference purposes. The washability curve is a type of cumulative curve on which can be read the concentration of an element that would be expected at any given rate of recovery of a coal, assuming a separation based on differences in specific gravity. Therefore, the abscissa is "recovery of float coal—percent" and should be applicable to any specific gravity separation, without regard to the medium in which it is done or the method used. The raw coal concentration of an element is read at the 100 percent recovery point, and concentration in the cleanest coals (most mineral-matter-free) is read at the low recovery end of the curve (20 to 30 percent recovery). All of the washability curves shown are drawn with the ordinates the same length and the origin at zero concentration. The slopes of the curves can therefore be compared and interpreted.

A positive slope of the washability curve shows that the element is concentrated in the inorganic (mineral matter) portion of the coal. Conversely, a negative slope demonstrates organic affinity for an element. Table 14 lists the trace elements in order of decreasing "organic" affinity. The sequence was determined by comparing ratios of the amount of an element in the lightest float fraction (always less than 1.30 specific gravity) to the amount of that element in the 1.60 sink fraction. The numerical values thus determined are not given since they will vary with the particle-size distribution of the coal, the specific gravity of the liquid used to make the first (lightest) separation, and the size distribution of the mineral fragments in a single coal. However, the sequence given in table 14 does indicate which elements are primarily in organic combination, which are in inorganic combination, and which are, apparently, both inorganically and organically combined in coals of the Illinois Basin.

The sequences shown in table 14 can be divided into several general groups. First, there are those elements which, when determined, are always in the group most closely associated with the clean coal and which, therefore,

(Continued on page 51)

TABLE 11—MAJOR AND MINOR ELEMENTS IN LABORATORY-PREPARED COALS
(percent, moisture-free coal)

SAMPLE NO.	SPECIFIC GRAVITY FRACTION*	PERCENT OF RAW COAL	COAL SEAM	AL	CA	FE	K	MG	NA	SI	TI
C-18090	3/8X28M	100,00	DV	0,91	0,21	2,70	0,14	0,040	0,010	2,11	0,06
C-18094	1,28F	25,87	DV	0,43	0,21	0,51	0,06	0,020	0,010	0,77	0,04
C-18095	1,30FS	19,50	DV	0,54	0,17	0,83	0,09	0,020	0,010	1,16	0,05
C-18096	1,32FS	19,70	DV	0,77	0,41	1,04	0,12	0,030	0,010	1,58	0,06
C-18097	1,40FS	19,30	DV	1,28	0,73	1,39	0,23	0,040	0,020	2,80	0,09
C-18098	1,60FS	7,20	DV	2,23	0,53	2,00	0,37	0,080	0,020	5,51	0,12
C-18099	>1,60	8,50	DV	1,39	0,41	26,10	0,07	0.170	0,020	3,62	0,04
C-18106	2,89FS	3,75	DV	4,21	0,49	6,92	0,25			8,27	0,11
C-18107	>2.90	4.75	DV	0,23	0,24	34,84			0,020		
C-18092	3/8X28M	100,00	DK	1,21	0,11	2,98	0,18	0,006	0,020	2,02	0,07
C-18100	1,29F	19,40	DK	0,53	0.18	0,86	0,08	0,003	0,010	0,78	0,04
C-18105	1.60S	9,00	DK	1.50	0,03	6,64	0,31	0,010	0,010	2,63	0,04
C-18134	28MX0	100,00	2	1.15	1.16	2,84	0,09	0,004	0,020	1,69	0,03
C-18133	3/8X28M	100,00	2	0,61	0,40	3,03	0,08	0,001	0,010	1,05	0,03
C-18135	1,25F	28,20	2	0,26	0,07	1,19	0,05	0,001	0,008	0,49	0,03
C-18136	1,26FS	23,60	2	0,28	0,07	1,54	0,05	0,001	0,008	0,58	0,03
C-18137	1,30FS	27,60	2	0,38	0,07	2,40	0,06	0,001	0,080	0,77	0,03
C-18138	1,40FS	10,60	2	0,87	0,08	3,10	0,11	0,003	0,010	1,53	0,05
C-18139	1,60FS	3,20	2	2,00	0,16	3,72	0,26	0,008	0,020	3,44	0,07
C-18140	>1,60	6,80	2	3,05	4,53	21,21	0,36	0,010	0,020	5,31	0,10
C-18141	2,89FS	3,60	2	6,19	7,85	16,00	0,76			11,41	0,19
C-18142	>2.90	3.20	2	0,33	0,70	29,67					
C-18122	28MX0	100.00	6	3,21	0,79	1,46	0,26	0,009	0,060	4,49	0,11
C-18121	3/8X28M	100,00	6	2,67	0,56	1,72	0,25	0,008	0,040	4,16	0,11
C-18123	1,25F	36,10	6	0,41	0,06	0,54	0,06	0,003	0,020	0,59	0,03
C-18124	1,29FS	17,40	6	0,52	0,05	0,72	0,09	0,003	0,020	0,87	0,05
C-18125	1,33FS	14,70	6	0,84	0,06	1,07	0,12	0,004	0,020	1,45	0,06
C-18126	1,40FS	9,30	6	1,43	0,08	1,61	0,20	0,006	0,040	2,52	0,09
C-18127	1,60FS	6,90	6	2,92	0,12	1,69	0,36	0,010	0,050	4,98	0,13
C-18128	>1,60	15,60	6	9,50	3,20	9,88	1,20	0,030	0,140	19,35	0,56
C-18129	2,89FS	12,73	6	11,89	4,27	5,19	1,44			23,19	0,65
C-18130	>2,90	2,87	6	1.93	0,11	35,13	0,07		0,040	2,89	0,09

* Specific gravity fractions given followed by the letters FS indicate that the entire sample would float at that gravity and would sink at the gravity listed immediately above.

TABLE 12—PROXIMATE ANALYSES AND ASH CONTENT OF LABORATORY-PREPARED COALS (percent, moisture-free, except for air-dry loss and moisture)

SAMPLE NO.	SPECIFIC GRAVITY FRACTION*	PERCENT OF RAW COAL	COAL SEAM	ADL	MOIS	VOL	FIXC	ASH	BTU	HTA	LTA
C-18090	3/8X28M	100,00	DV	1,9	2,7	38,1	51,0	10,9	13311	10,90	15,80
C-18094	1,28F	25,87	DV	0,5	1,3					3,00	3,61
C-18095	1,30FS	19,50	DV	0,6	1,3					3,90	5,68
C-18096	1,32FS	19,70	DV	1,4	2,1					5,40	6,67
C-18097	1,40FS	19,30	DV	0,3	1,3					9,40	12,74
C-18098	1,60FS	7,20	DV		1,0					19,80	23,06
C-18099	>1,60	8,50	DV	0,1	0,8					51,40	73,53
C-18106	2,89FS	3,75	DV		3,1					39,20	47,76
C-18107	>2,90	4,75	DV		0,6					61,00	92,66
C-18092	3/8X28M	100,00	DK	2.40	3,20	38,00	48,60	13,40	12745	13,40	15,73
C-18100	1,29F	19,40	DK	0.20	1,10					5,40	4,79
C-18105	1,60S	9.00	DK		0.40					49.80	74.07
C-18134	28MX0	100,00	2	10,30	12,00					16,60	20,15
C-18133	3/8X28M	100,00	2	10,90	13,10	41,50	47,40	11,00	12740	11,00	15,57
C-18135	1,25F	28,20	2	10,00	11,90					2,60	3,56
C-18136	1,26FS	23,60	2	8,00	9,90					3,50	6,30
C-18137	1,30FS	27,60	2	7,40	9,50					5,00	9,48
C-18138	1,40FS	10,60	2	7,00	9,10					10,50	16,21
C-18139	1,60FS	3,20	2	3,10	5,00					21,70	28,75
C-18140	>1,60	6,80	2	0,70	1,50					56,50	78,20
C-18141	2,89FS	3,60	2		4,40					46,90	60,14
C-18142	>2.90	3.20	2		0.30					65,00	99,61
C-18122	28MX0	100,00	6	9,50	10,80					23,80	28,23
C-18121	3/8X28M	100,00	6	11,30	12,90	37,80	41,50	20,70	11256	20,70	26,28
C-18123	1,25F	36,10	6	7,90	9,90					3,10	3,83
C-18124	1,29FS	17,40	6	8,60	10,50					3,70	5,01
C-18125	1,33FS	14,70	6	5,20	7,30					6,10	8,18
C-18126	1,40FS	9,30	6	3,70	5,40					11,20	14,86
C-18127	1,60FS	6,90	6	1,90	3,70					21,90	25,92
C-18128	>1,60	15,60	6	1,20	2,10					72,80	88,40
C-18129	2,89FS	12,73	6		1,00					75,20	86,02
C-18130	>2,90	2,87	6		0,20					65,60	98,71

* Specific gravity fractions given followed by the letters FS indicate that the entire sample would float at that gravity and would sink at the gravity listed immediately above.

Air-dry loss (ADL), moisture (MOIS), high-temperature ash (HTA), low-temperature ash (LTA).

TABLE 13—SULFUR ANALYSIS OF LABORATORY PREPARED COALS
(percent, moisture-free)

SAMPLE NO.	SPECIFIC GRAVITY FRACTION*	PERCENT OF RAW COAL	COAL SEAM	ORS	PYS	SUS	TOS	SXRF
C-18090	3/8X28M	100,00	DV	1,17	3,25	0,01	4,43	3,21
C-18094	1,28F	25,87	DV	1,20	0,40	0,0	1,60	2,37
C-18095	1,30FS	19,50	DV	1,19	0,45	0,0	1,64	2,29
C-18096	1,32FS	19,70	DV	1,21	0,62	0,0	1,83	2,32
C-18097	1,40FS	19,30	DV	1,26	1,04	0,0	2,30	2,20
C-18098	1,60FS	7,20	DV	1,11	2,47	0,0	3,59	2,17
C-18099	>1,60	8,50	DV	0,02	29,26	0,10	29,39	29,39
C-18106	2,89FS	3,75	DV	2,03	9,09	0,10	11,23	
C-18107	>2,90	4,75	DV	1,24	44,23	0,15	45,42	
C-18092	3/8X28M	100,00	DK	0,76	4,73	0,01	5,50	3,25
C-18100	1,29F	19,40	DK	0,96	1,52	0,01	2,49	1,89
C-18105	1.60S	9.00	DK	0.24	31.20	0,15	31.60	11.48
C-18134	28MX0	100,00	2	1,28	4,79	0,04	6,11	3,28
C-18133	3/8X28M	100,00	2	1,27	4,38	0,03	5,68	3,68
C-18135	1,25F	28,20	2	1,19	0,78	0,20	1,98	2,17
C-18136	1,26FS	23,60	2	1,00	1,09	0,02	2,11	2,40
C-18137	1,30FS	27,60	2	1,03	2,08	0,03	3,14	3,21
C-18138	1,40FS	10,60	2	1,16	3,98	0,06	5,19	3,76
C-18139	1,60FS	3,20	2	0,96	6,84	0,08	7,88	3,89
C-18140	>1,60	6,80	2	0,01	27,46	0,15	27,62	27,00
C-18141	2,89FS	3,60	2	0,01	12,94	0,13	13,08	
C-18142	>2,90	3,20	2	0.01	45.81	0.04	45.86	
C-18122	28MX0	100,00	6	1,56	2,17	0,04	3,76	2,32
C-18121	3/8X28M	100,00	6	1,70	2,23	0,03	3,96	2,81
C-18123	1,25F	36,10	6	1,60	0,46	0,02	2,07	3,04
C-18124	1,29FS	17,40	6	1,61	0,57	0,02	2,20	3,07
C-18125	1,33FS	14,70	6	1,47	0,97	0,03	2,46	3,10
C-18126	1,40FS	9,30	6	1,26	1,75	0,03	3,04	3,11
C-18127	1,60FS	6,90	6	1,43	2,13	0,03	3,60	2,52
C-18128	>1,60	15,60	6	0,61	9,90	0,08	10,59	2,16
C-18129	2,89FS	12,73	6	0,30	1,44	0,31	2,05	
C-18130	>2,90	2.87	6	0,01	42,96	0,12	43,09	

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* Specific gravity fractions given followed by the letters FS indicate that the entire sample would float at that gravity and would sink at the gravity listed immediately above.

Organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF).

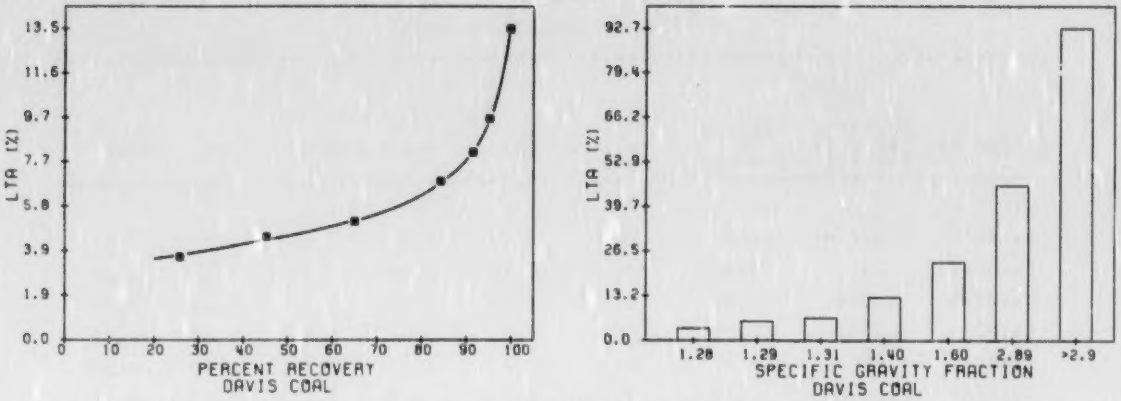

Fig. 40 - Low-temperature ash in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of LTA in individual fractions.

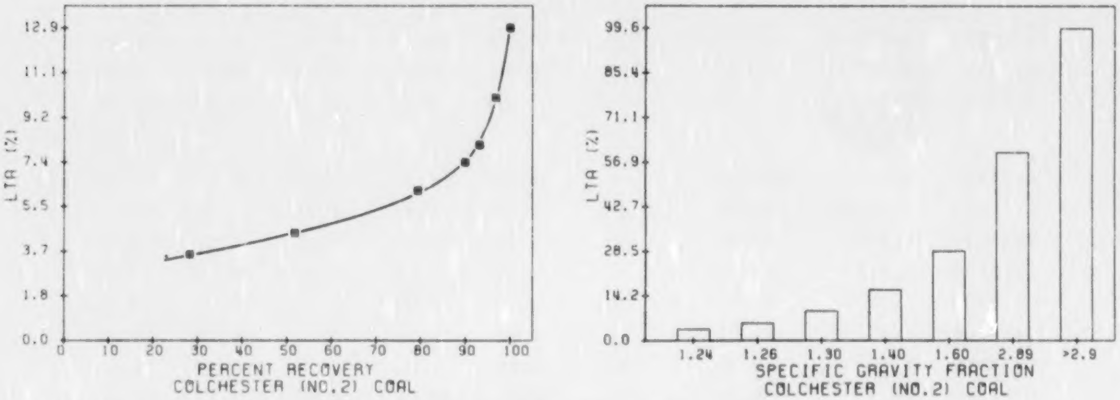

Fig. 41 - Low-temperature ash in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of LTA in individual fractions.

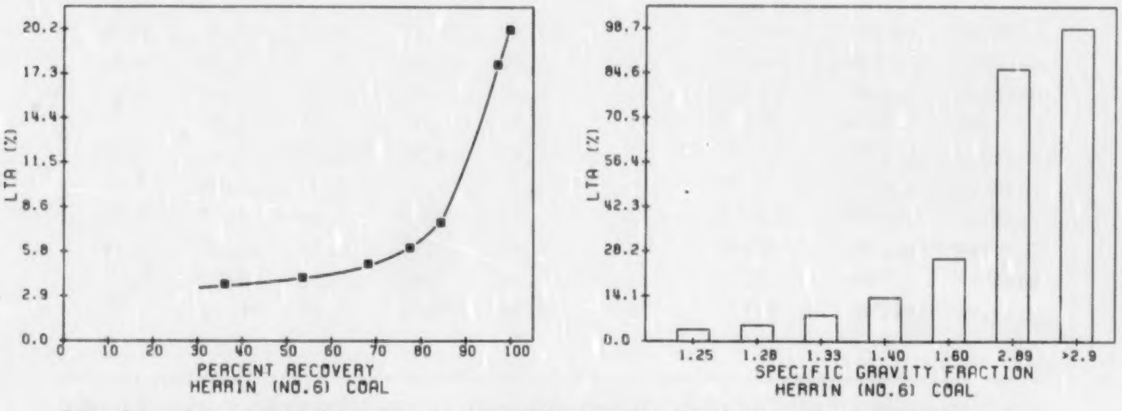

Fig. 42 - Low-temperature ash in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of LTA in individual fractions.

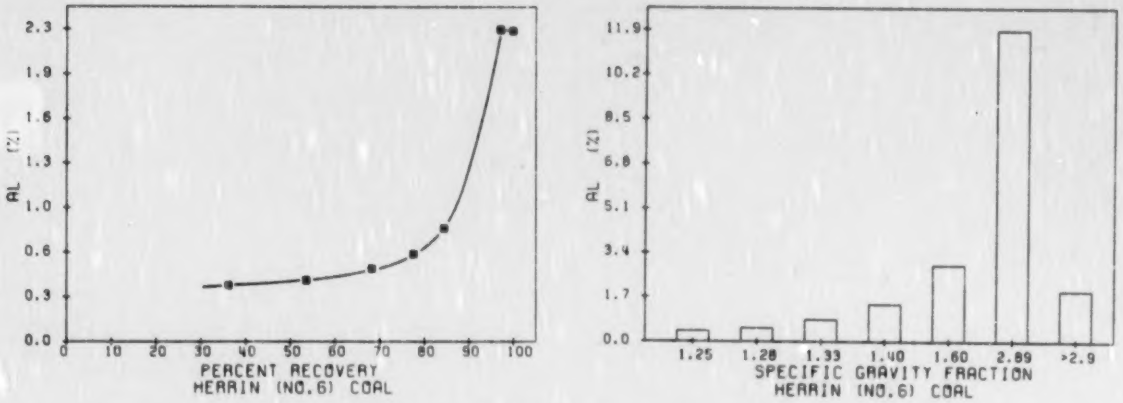

Fig. 43 - Aluminum in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of aluminum in individual fractions.

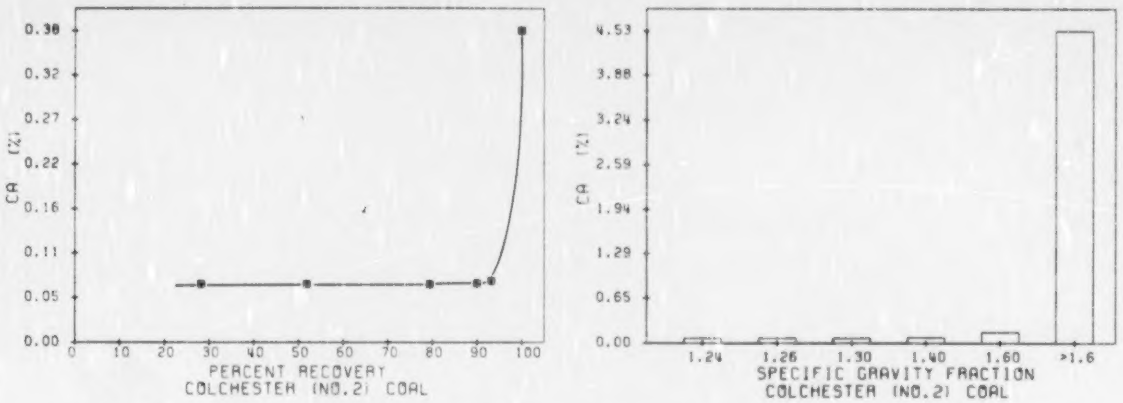

Fig. 44 - Calcium in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of calcium in individual fractions.

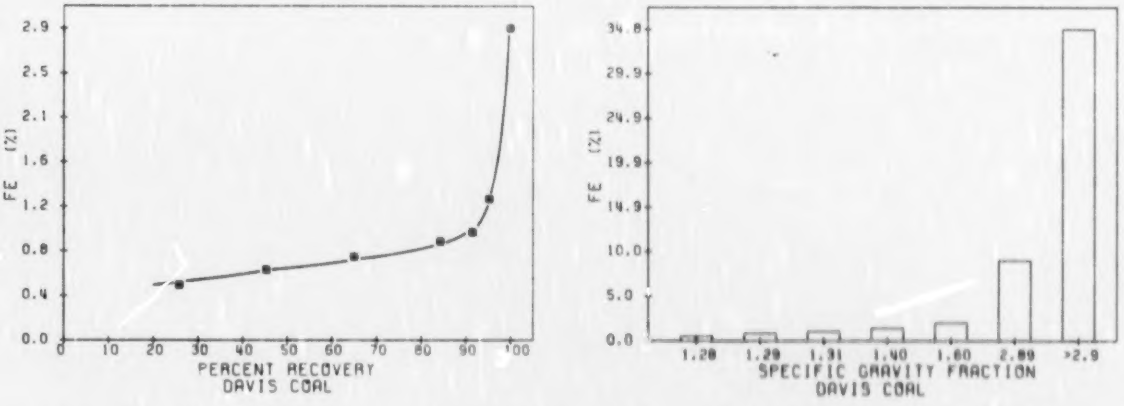

Fig. 45 - Iron in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of iron in individual fractions.

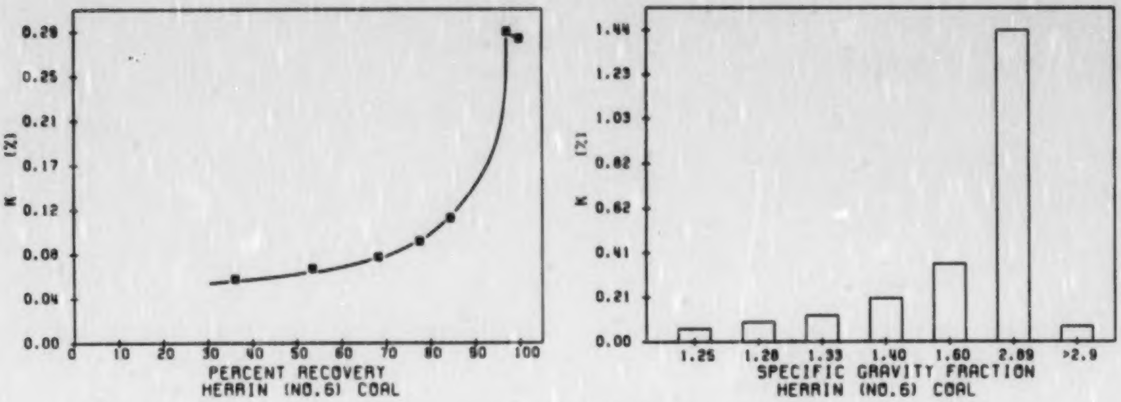

Fig. 46 - Potassium in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of potassium in individual fractions.

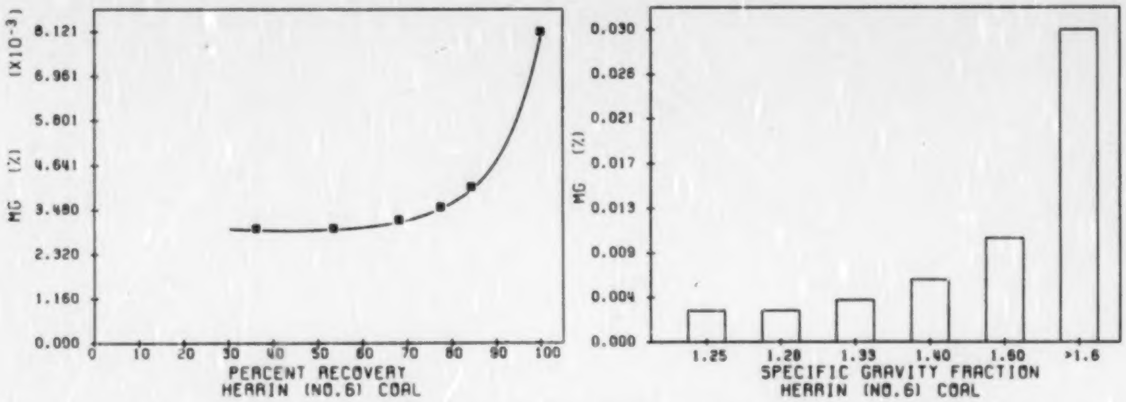

Fig. 47 - Magnesium in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of magnesium in individual fractions.

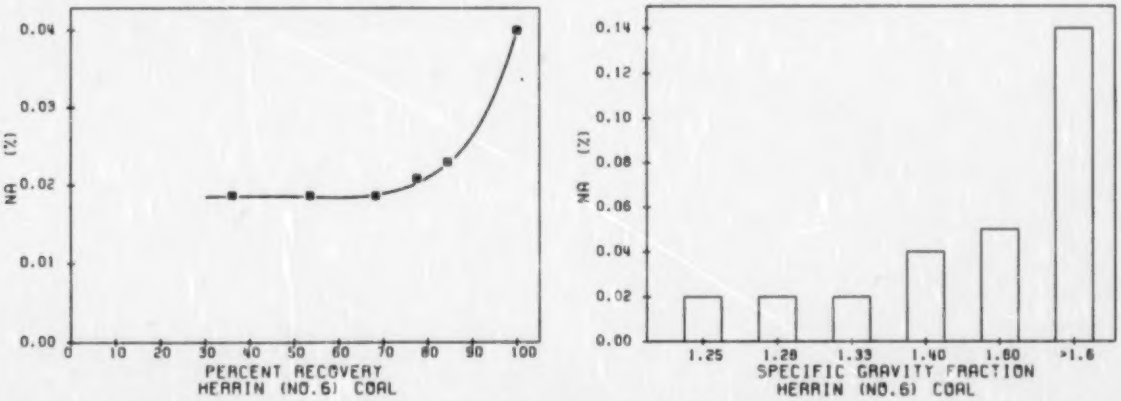

Fig. 48 - Sodium in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of sodium in individual fractions.

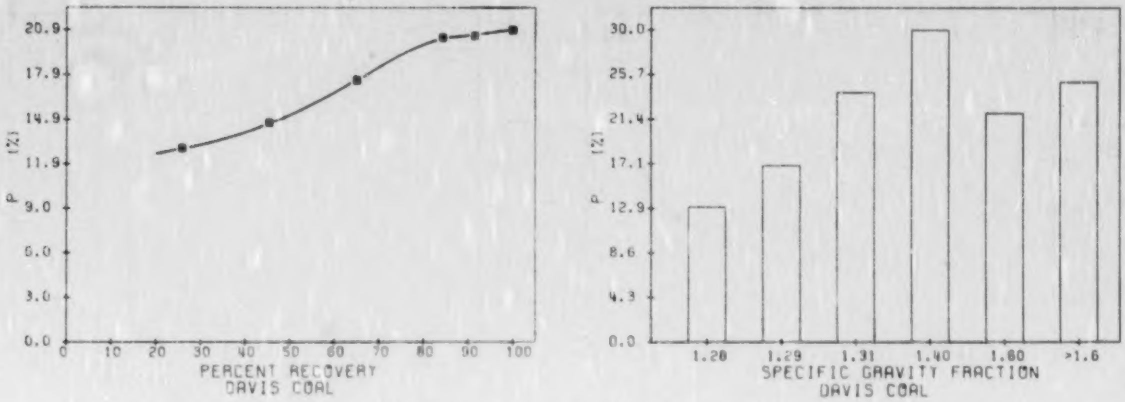

Fig. 49 - Phosphorus in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of phosphorus in individual fractions.

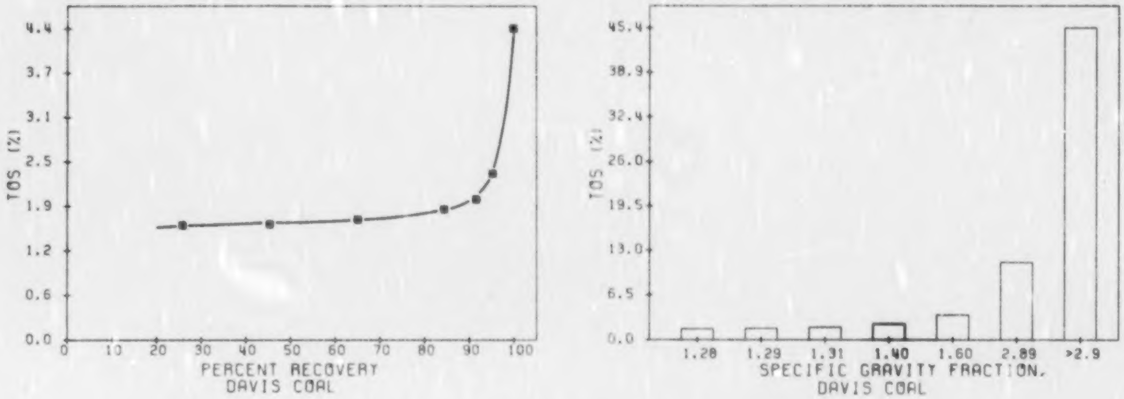

Fig. 50 - Sulfur in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of sulfur in individual fractions.

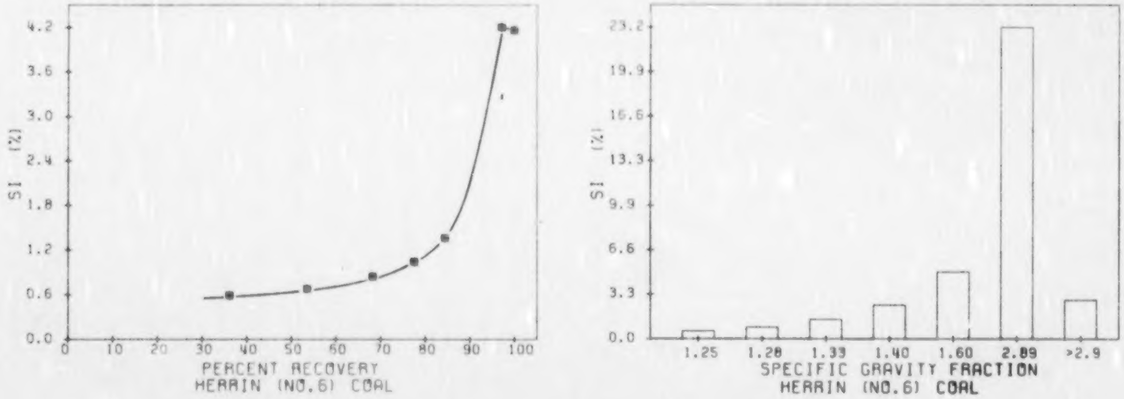

Fig. 51 - Silicon in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of silicon in individual fractions.

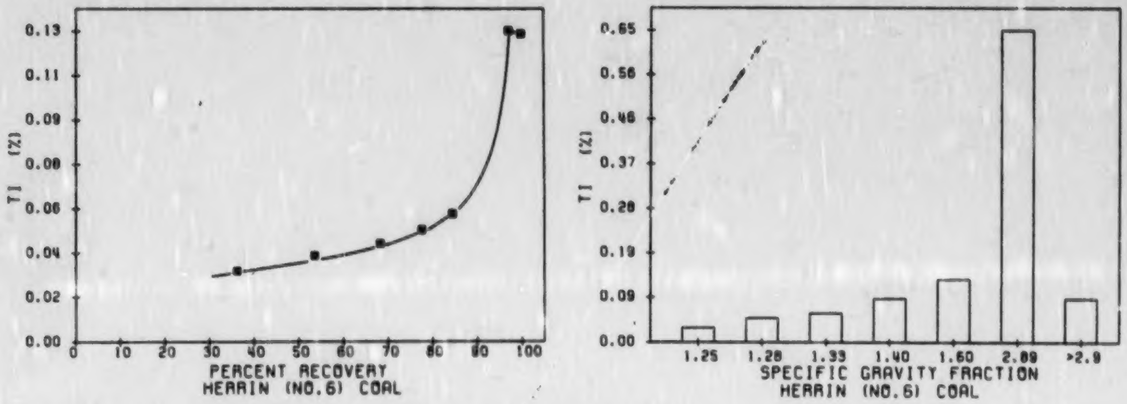

Fig. 52 - Titanium in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of titanium in individual fractions.

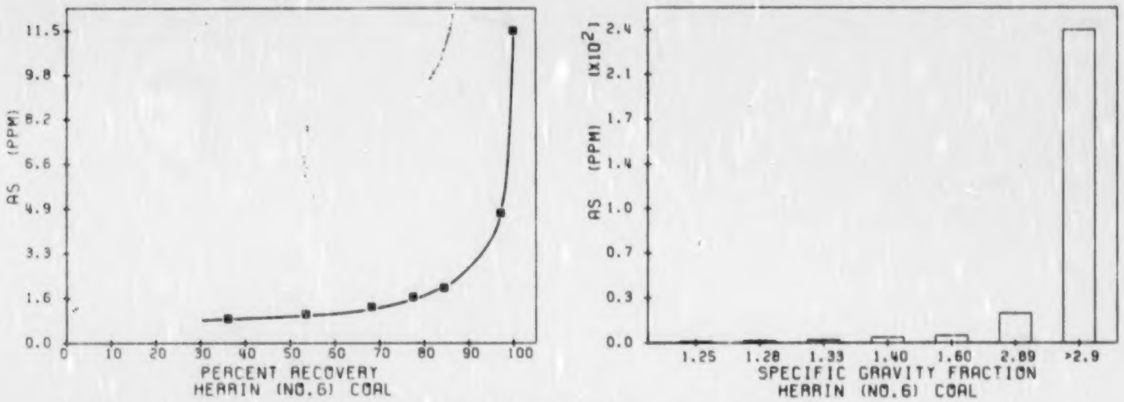

Fig. 53 - Arsenic in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of arsenic in individual fractions.

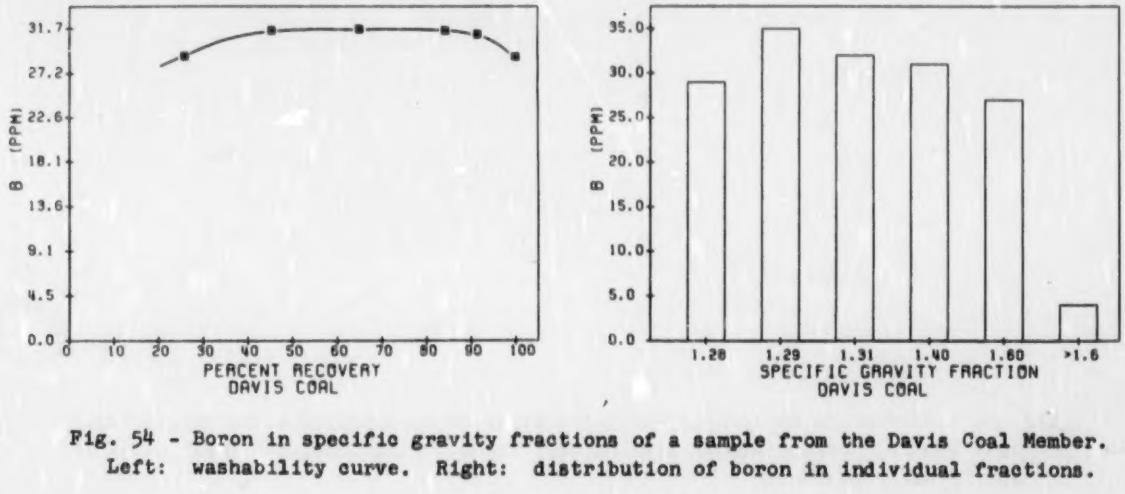

Fig. 54 - Boron in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of boron in individual fractions.

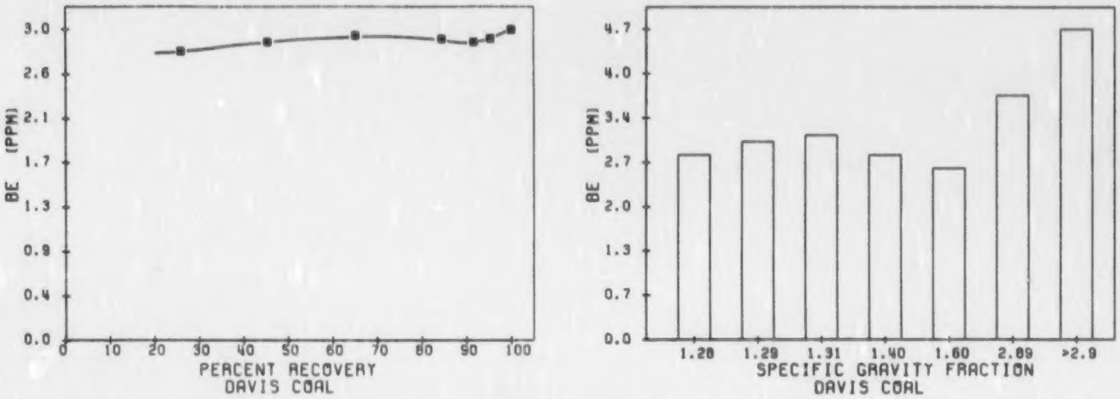

Fig. 55 - Beryllium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of beryllium in individual fractions.

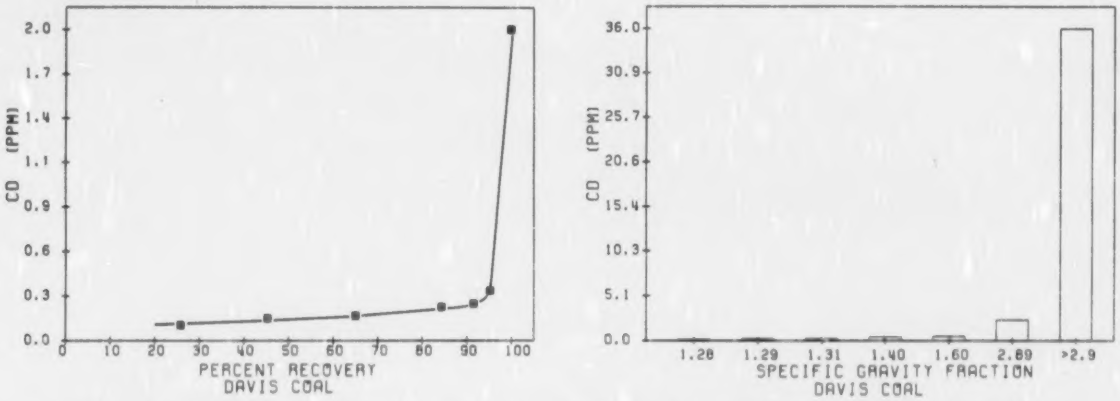

Fig. 56 - Cadmium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of cadmium in individual fractions.

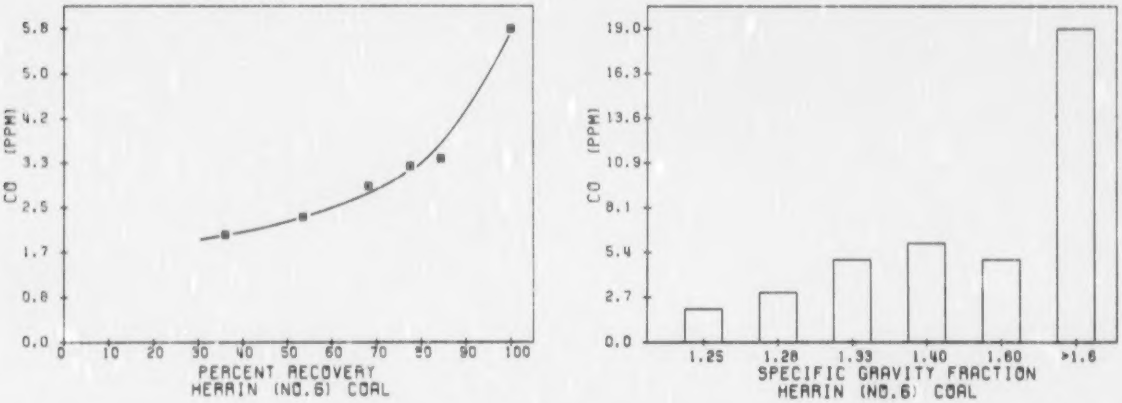

Fig. 57 - Cobalt in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of cobalt in individual fractions.

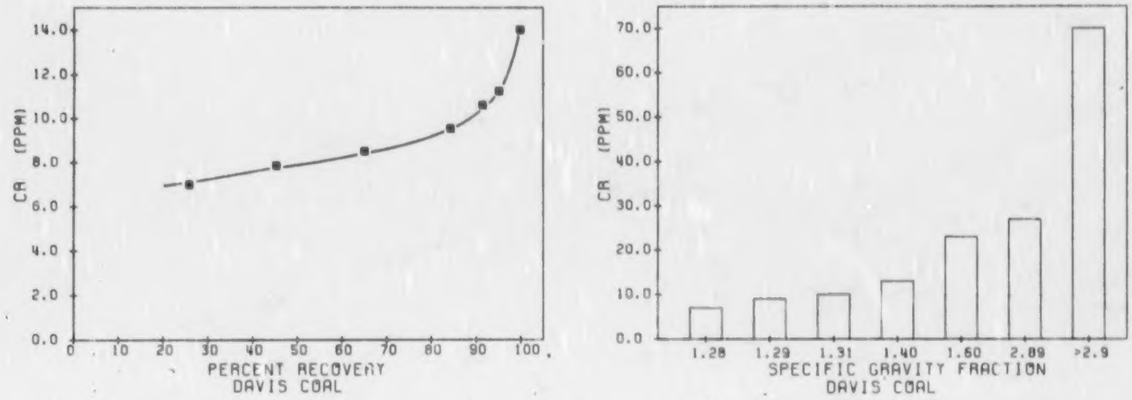

Fig. 58 - Chromium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of chromium in individual fractions.

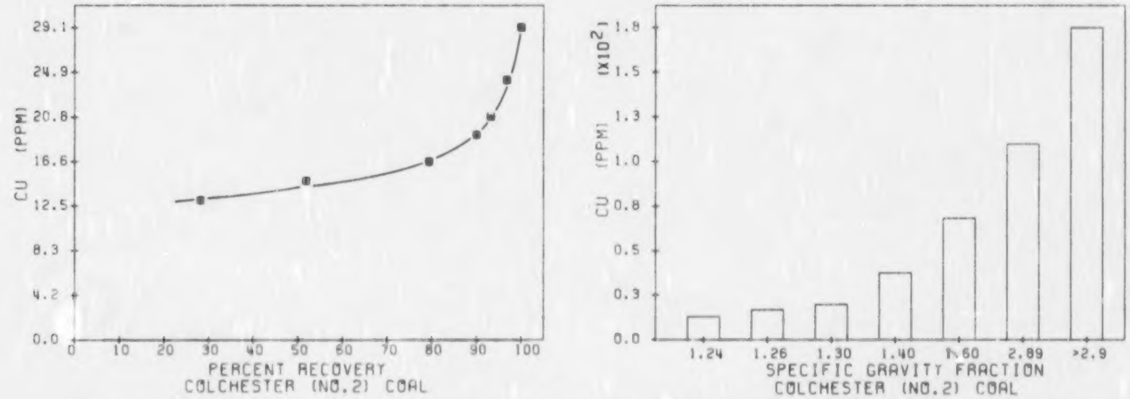

Fig. 59 - Copper in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of copper in individual fractions.

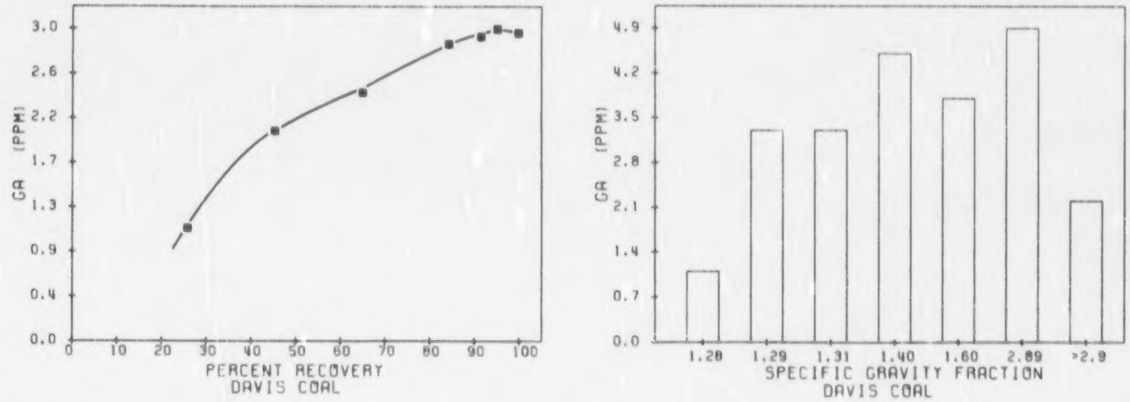

Fig. 60 - Gallium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of gallium in individual fractions.

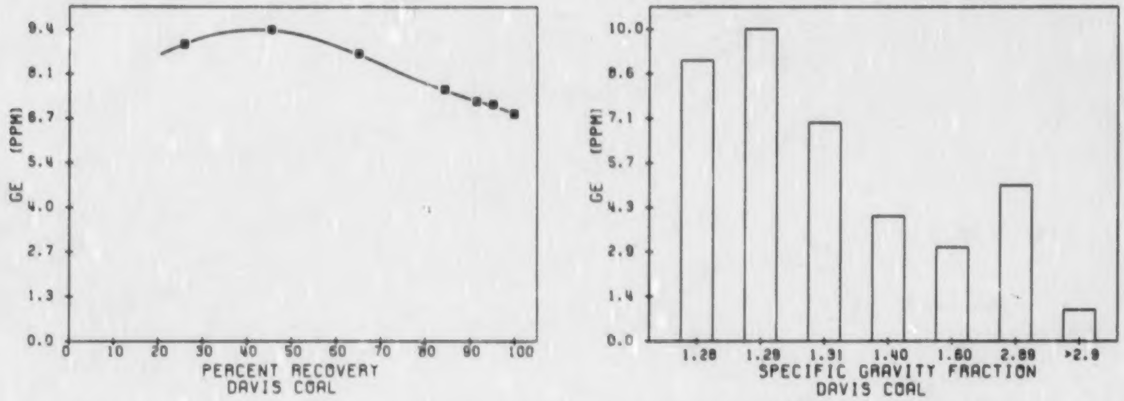

Fig. 61 - Germanium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of germanium in individual fractions.

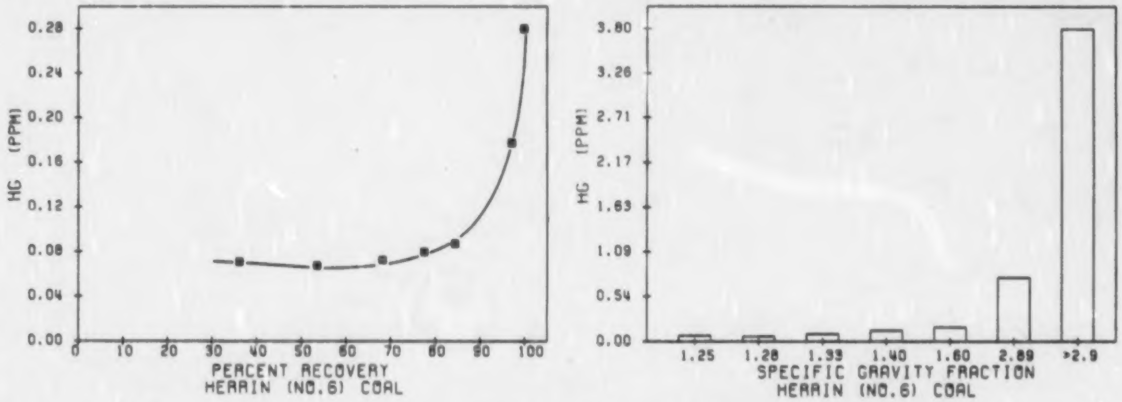

Fig. 62 - Mercury in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of mercury in individual fractions.

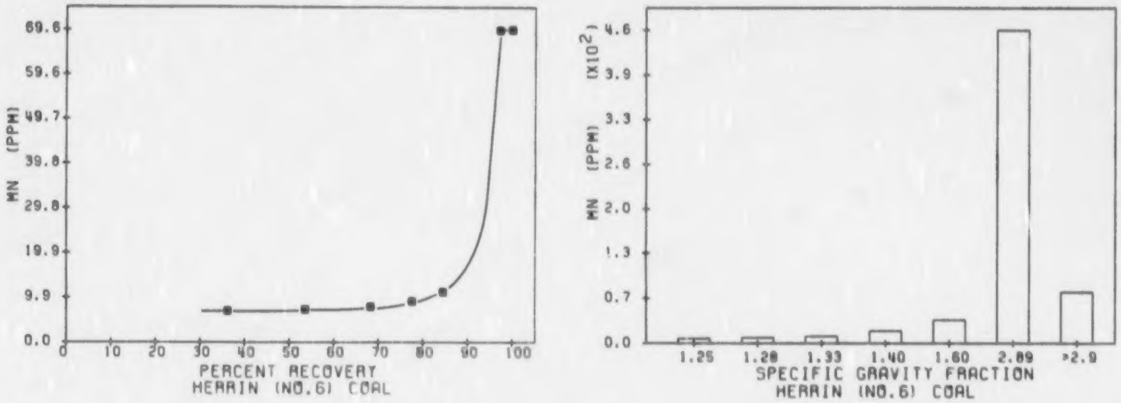

Fig. 63 - Manganese in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of manganese in individual fractions.

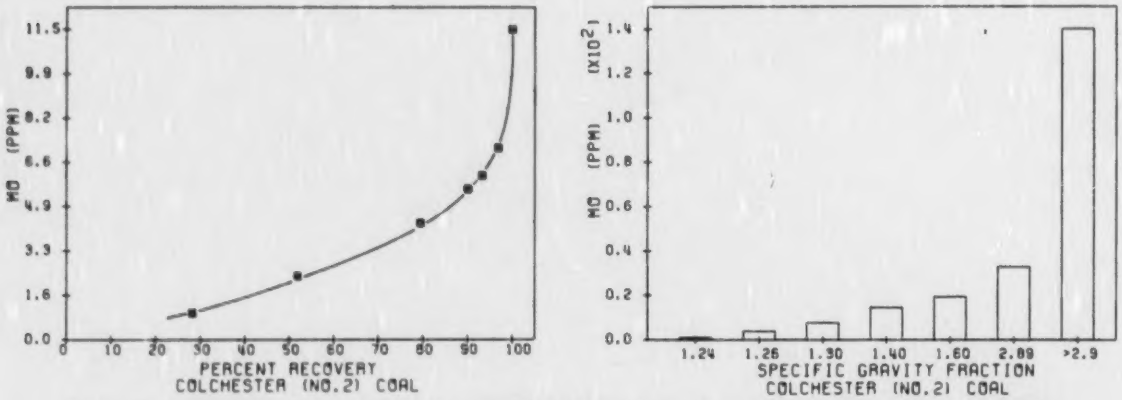

Fig. 64 - Molybdenum in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of molybdenum in individual fractions.

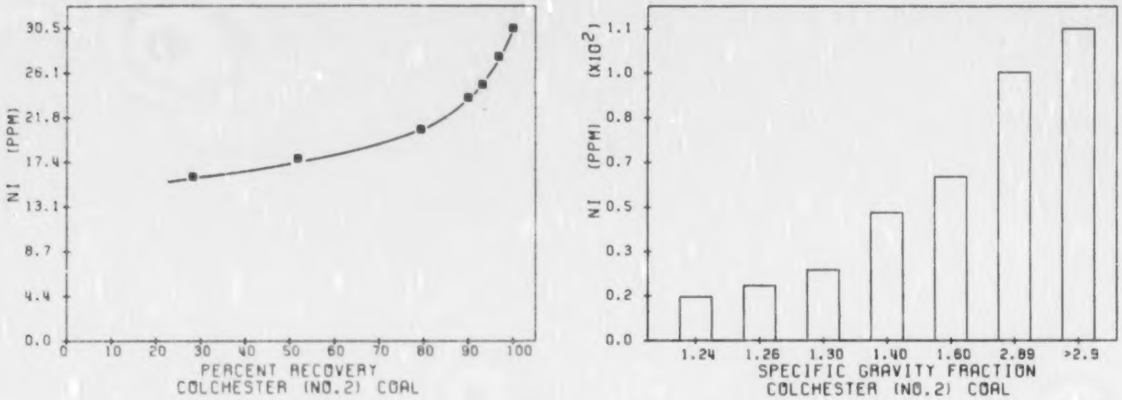

Fig. 65 - Nickel in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of nickel in individual fractions.

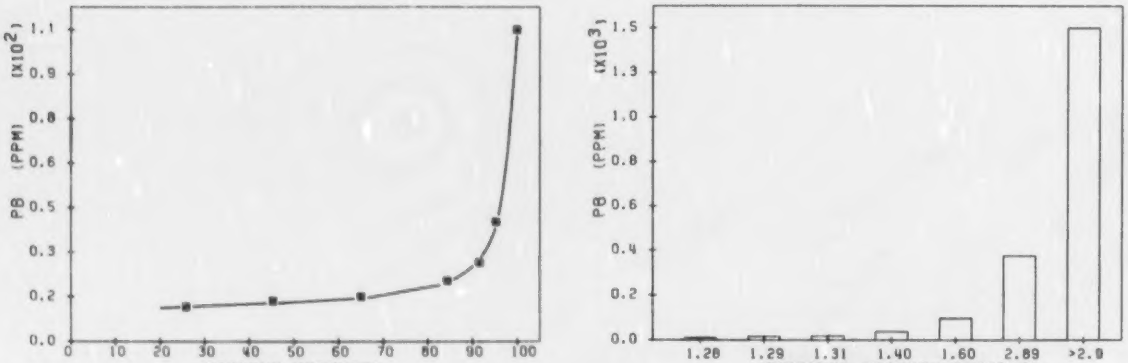

Fig. 66 - Lead in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of lead in individual fractions.

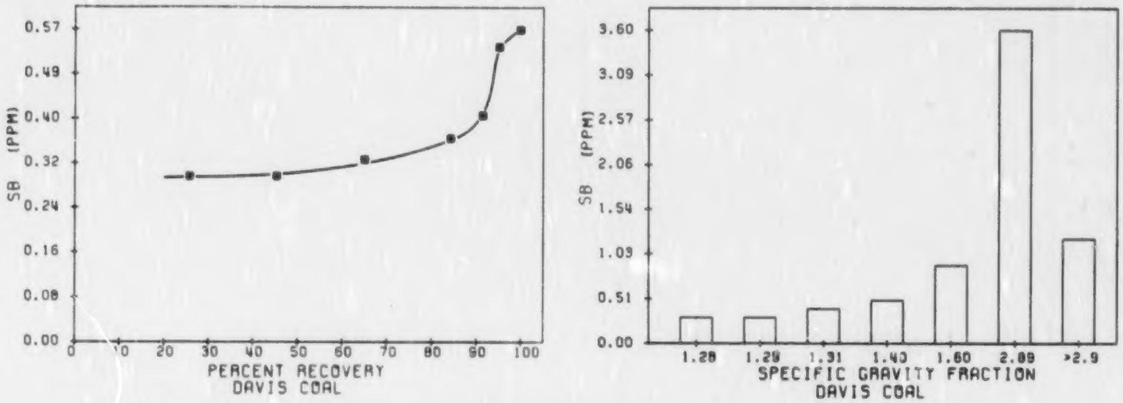

Fig. 67 - Antimony in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of antimony in individual fractions.

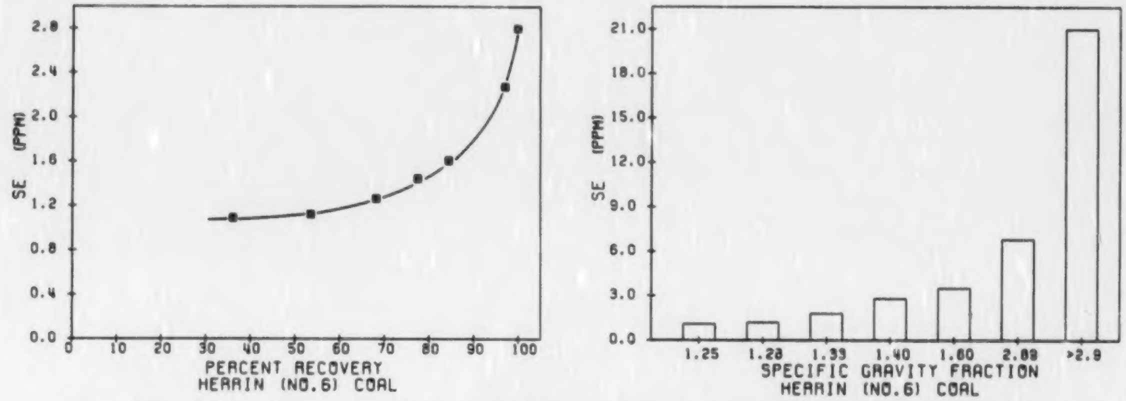

Fig. 68 - Selenium in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of selenium in individual fractions.

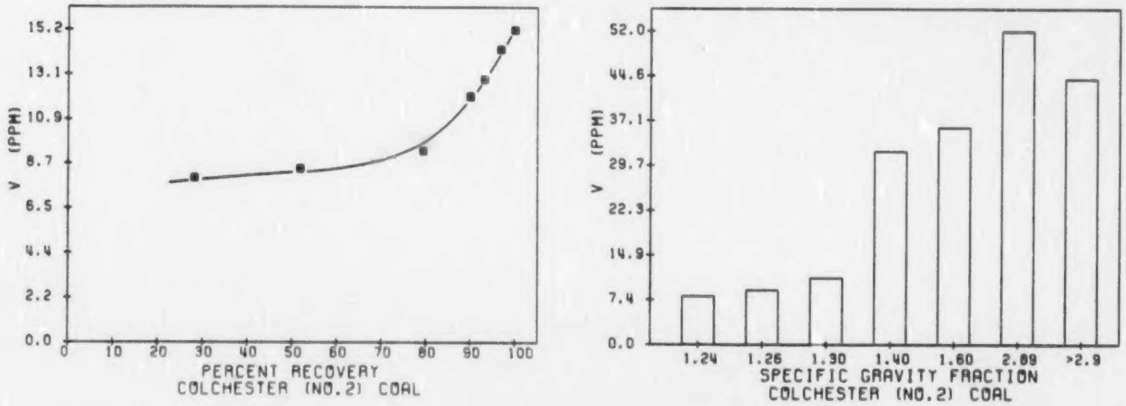

Fig. 69 - Vanadium in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of vanadium in individual fractions.

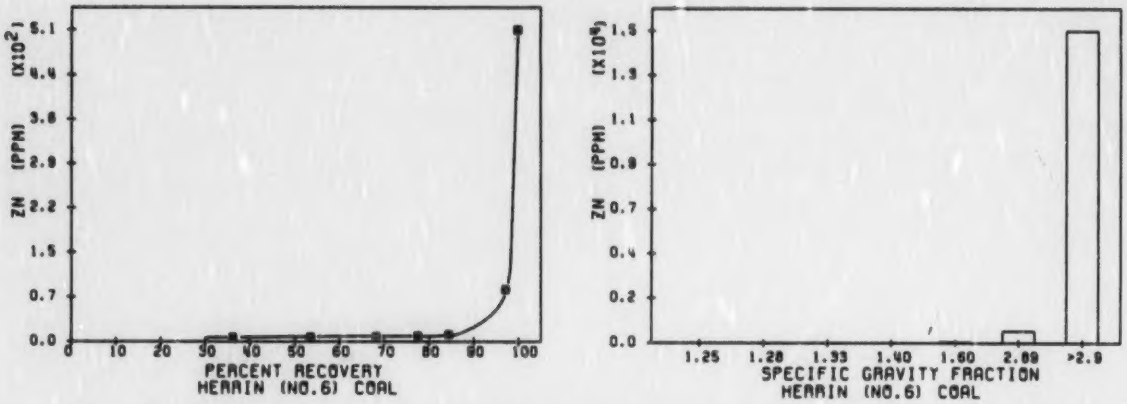

Fig. 70 - Zinc in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: washability curve. Right: distribution of zinc in individual fractions.

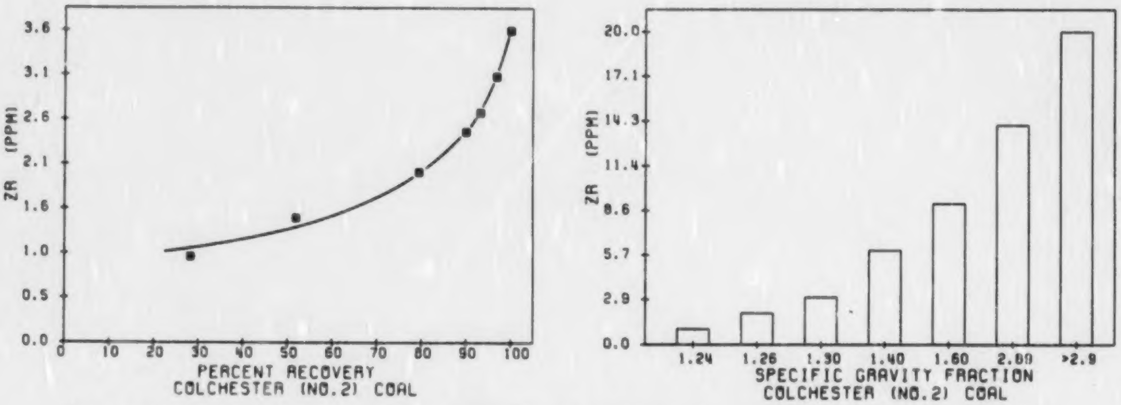

Fig. 71 - Zirconium in specific gravity fractions of a sample from the Colchester (No. 2) Coal Member. Left: washability curve. Right: distribution of zirconium in individual fractions.

TABLE 14—AFFINITY OF ELEMENTS FOR PURE COAL AND FOR MINERAL MATTER, AS DETERMINED FROM FLOAT-SINK DATA

	Davis Coal	DeKoven Coal	Colchester (No. 2) Coal	Herrin (No. 6) Coal
Clean coal - lightest specific gravity fraction (elements in "organic combination")	B	Ge	Ge	Ge
	Ge	Ga	B	B
	Be	Be	P	Be
	Ti	Ti	Be	Sb
	Ga	Sb	Sb	V
	P	Co	Ti	Mo
	V	P	Co	Ga
	Cr	Ni	Se	P
	Sb	Cu	Ga	Se
↕	Se	Se	V	Ni
	Co	Cr	Ni	Cr
	Cu	Mn	Pb	Co
	Ni	Zn	Cu	Cu
	Mn	Zr	Hg	Ti
	Zr	V	Zr	Zr
	Mo	Cd	Cr	Pb
	Cd	Mo	Mn	Mn
Mineral matter - specific gravity greater than 1.60 (elements in "inorganic combination")	Hg	Pb	As	As
	Pb	Hg	Mo	Cd
	Zn	As	Cd	Zn
	As		Zn	Hg

have the greatest organic affinities. These are Ge, Be, and B, which are three of the top five elements listed by Zubovic (1966, p. 222) in similar analyses of trace element data. At the other end of the list are the elements with the least affinity for the organic portion of the coal. The elements Hg, Zr, Zn, As, and Cd are near the bottom in all four coals studied, and Pb, Mn, and Mo are near the bottom in three of the four. The remaining elements, those that are apparently associated, to varying degrees, with both the organic and inorganic portions of the coals can also be divided into two groups: those elements that tend to be more generally allied to the elements with organic affinities (P, Ga, Sb, Ti, and V), and those elements that tend to be more inorganically associated (Co, Ni, Cr, Se, and Cu). A comparison of this summarized sequence with that given by Zubovic (1966, p. 222) shows generally good agreement, with only a few minor discrepancies. The elements listed in table 1 include 12 of the 15 elements discussed by Zubovic (1966) as well as nine additional elements.

Although an element may be listed among those with the highest organic affinities, its occurrence in inorganic combination in coals is not precluded. Boron, which is among those found in high concentrations in the cleanest coal fractions, is known to occur in amounts up to 200 ppm in the clay mineral illite from Illinois coals (Bohor and Gluskoter, 1973). Similarly, a portion of those elements usually concentrated most heavily in the high specific gravity fractions may also be in organic combination. This dual mode of occurrence was postulated for the Hg content of Illinois coals by Ruch, Gluskoter, and Kennedy (1971), and mercury is included here with the elements having lower organic affinities. The shapes of the washability curves for Mg, Na, Co, Cr, Cu, Ga, Ni, Sb, Se, and V all suggest at least a partial organic contribution. They all have positive slopes, showing that those elements are concentrated in the mineral matter, but all of the curves flatten out at some distance above the base-line and, if extrapolated to zero percent recovery, would intersect the ordinate well above the origin. These elements all have curves which are flatter than the LTA curve for the same set of coal samples and more nearly resemble the washability curve for total sulfur (TOS) in the Davis Coal Member (fig. 50). The total sulfur in the whole coal (raw, or unwashed) 3/8 inch by 28 mesh Davis Coal sample is composed of 0.07 percent sulfate sulfur, 1.17 percent organic sulfur, and 3.25 percent pyritic sulfur; thus it contains a little more than 25 percent of the sulfur in organic combination.

Concentration of an element in the heavier fractions shows that element to be in inorganic combination. In the cases in which the final separation was done in bromoform (2.89 s.g.), we can postulate further on the mode of occurrence of certain elements. Si, Ti, Al, and K are all concentrated in the gravity fraction from 1.60 to 2.89 and are less abundant in the gravity fraction greater than 2.89. These elements are found associated with each other in the clay minerals and not in the heavier sulfides. Fe, S, As, Hg, Mo, Pb, Cd, and Zn are all concentrated in the heaviest gravity fractions (s.g. > 2.89) and are very likely present as sulfide minerals.

IDENTIFICATION OF MINERAL PHASES CONTAINING TRACE ELEMENTS

During the past few years several reports which describe investigations concerned with the origin, distribution, and mode of occurrence of mineral matter in Illinois coals have been published (Gluskoter, 1967; Gluskoter, Pierard, and Pfefferkorn, 1970; Gluskoter and Ruch, 1971; Rao and Gluskoter, 1973; and Gluskoter and Lindahl, 1973).

Certain of the trace elements determined in coals occur in discrete mineral phases. The identification of those minerals is therefore important. Identifying minerals in the low-temperature ash of coals is generally done by X-ray diffraction analysis, but the technique may not be sufficiently sensitive to identify very small quantities of a mineral. However, greater sensitivity may be achieved by using a scanning electron microscope (SEM) and the nondispersive X-ray analytical equipment that is an accessory to the SEM; in this way many of the minerals can be identified, even if they are present in very small quantities (pl. 1).

Plate 1 - Scanning electron photomicrographs of minerals in coals.

A. Calcite ($CaCO_3$) from cleat filling in Herrin (No. 6) Coal Member.
B. Kaolinite (aluminosilicate) from cleat filling in Herrin (No. 6) Coal Member.
C. Pyrite (FeS_2) framboids in low-temperature ash of DeKoven Coal Member.
D. Sphalerite (ZnS, also contains cadmium) from low-temperature ash of Herrin (No. 6) Coal Member.
E. Galena (PbS) from low-temperature ash of DeKoven Coal Member.
F. Apatite (calcium phosphate mineral) from low-temperature ash of coal sample from Colorado.

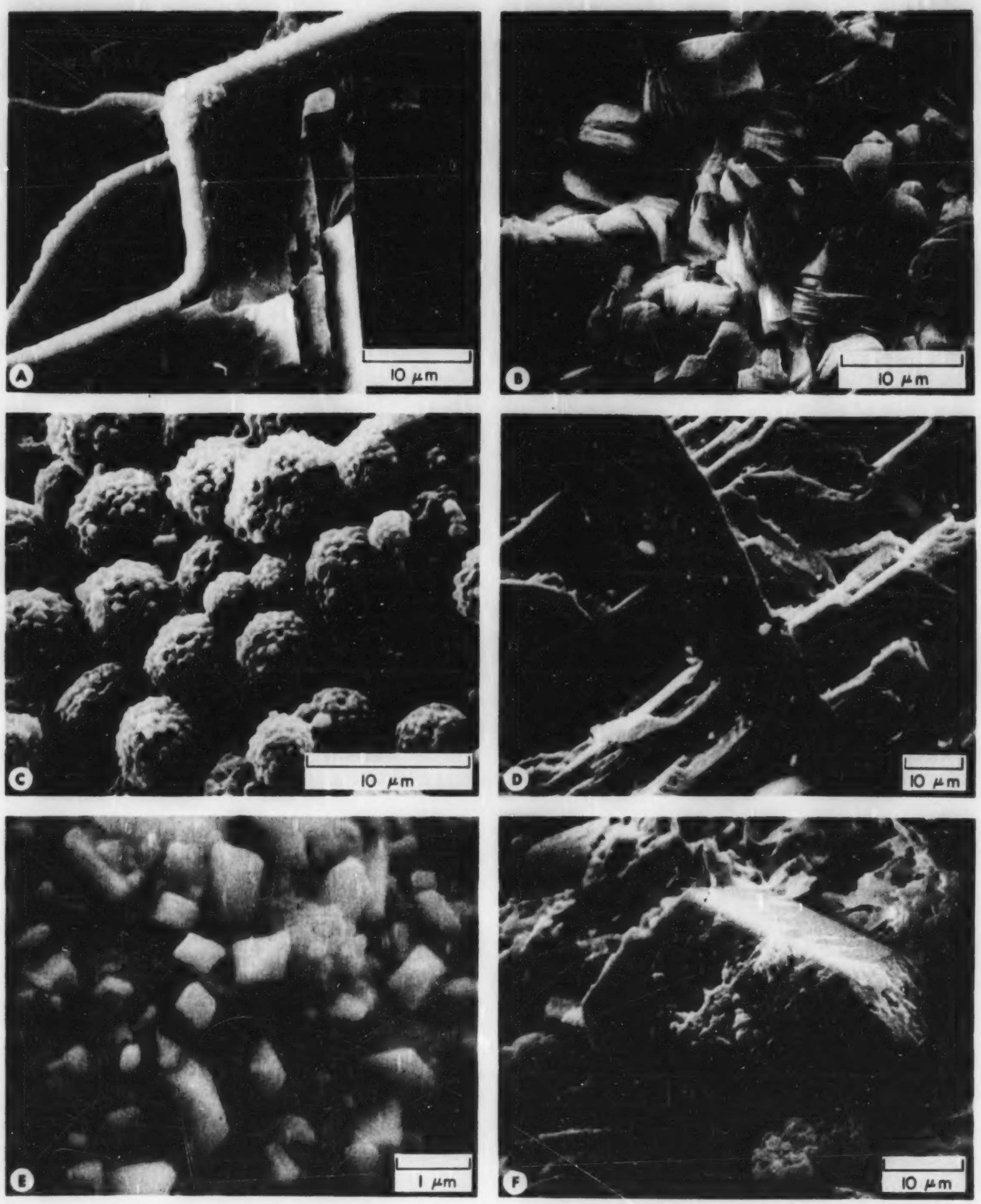
A
10 μm
B
10 μm
C
10 μm
D
10 μm
E
1 μm
F
10 μm

Plate 1

Sphalerite (ZnS) has been identified as the host mineral for Zn and Cd in the low-temperature ash of many coal samples from both the Illinois Basin (Illinois, Indiana, and western Kentucky) and Missouri. The distribution of Zn in coals of the Illinois Basin is presented in a published abstract (Gluskoter, Hatch, and Lindahl, 1973), and a more complete article describing the occurrence of sphalerite in coals is in preparation. The mode of occurrence of the cadmium in Illinois coals has also been described recently (Gluskoter and Lindahl, 1973). The sphalerite has been found in relatively large, discrete grains (pl. 1, D), and as the specific gravity of sphalerite is greater than 4, the mineral could be removed if the coal were washed (separated by specific gravity techniques).

The low-temperature ash from a coal sample from Colorado (C-17097) that has a relatively high P content was studied to identify the mineral phase containing the P. The mineral phase contained Ca in addition to P (pl. 1, F). A calcium phosphate mineral was also identified in the sample of an Illinois coal (C-15448) which contained 143 ppm F, the highest concentration of fluorine in the coals analyzed. Apatite (generally carbonate-fluorapatite) has been reported associated with coals; therefore, it is reasonable to assume that the mineral we have observed is apatite.

A separate phase containing lead has also been observed in the very fine fraction (less than 74 µm) of the low-temperature ash of a sample of the DeKoven Coal Member (C-15944). Although the X-radiation cannot be used to definitely identify sulfur in the presence of Pb, the crystal structure of the mineral and its mode of occurrence (pl. 1, E) indicate that the mineral is galena (PbS).

Other elements which have been identified in intimate association with pyrite (FeS_2) are nickel and copper (pl. 1, C). The identification of additional chalcophile elements which are in close association with pyrite requires more sensitive analytical equipment and improved sample preparation techniques.

SUMMARY AND CONCLUSIONS

Complete chemical analyses of 101 whole coal samples and of 32 laboratory-prepared samples, obtained by specific gravity separations of four coals, have been made in the laboratories of the Illinois State Geological Survey. Trace elements determined were Sb, As, Be, B, Br, Cd, Cr, Co, Cu, F, Ga, Ge, Pb, Mn, Mo, Ni, Hg, P, Se, Sn, V, Zn, and Zr. In addition, the following major and minor elements were also determined: Al, Ca, Cl, Fe, Mg, K, Si, Na, S, and Ti. Standard coal analyses—proximate, ultimate, heating value, varieties of sulfur, and ash—are also reported.

Procedures for the analytical methods used—neutron activation, optical emission, atomic absorption, X-ray fluorescence, and ion-selective electrode—are given in detail in the appendix.

Wherever possible, accuracy was evaluated by comparing results obtained by the various methods from representative splits of a coal sample. Further comparisons were made by analyzing whole coal and its low- and high-temperature ashes, thus permitting a thorough evaluation of trace element losses resulting from volatilization during sample preparation.

Generally, the results of the various analytical procedures compared favorably, although exceptions are noted, e.g., for V and F. Certain techniques have been chosen as preferred methods for determining specific elements because they are more accurate, their precision is superior, or they take less time for analysis.

Eighty-two of the 101 whole coal samples were from the Illinois Basin (Illinois, Indiana, and western Kentucky). The additional 19 samples were from other areas of the United States. The four samples which were prepared in the laboratory (washed) were also from the Illinois Basin.

As a first step in the statistical analyses of the more than 6,000 analytical values generated (there were as many as 50 separate determinations done on a single coal sample), arithmetic means, standard deviations, ranges, and linear correlation coefficients were calculated on the trace elements, major elements, high- and low-temperature ashes, and the proximate and ultimate coal analyses for the 101 coals tested.

On the basis of these statistical calculations and of histograms of the element distributions, the elements can be grouped with those of similar type. One group displays a relatively normal distribution of analytical values, and elements within this group have small standard deviations and ranges. Included in this group are Al, F, Fe, Ga, Be, Br, B, Cr, Cu, K, Ni, Si, Ti, Se, and V. Elements in the second group all have a skewed pattern of analytical values, with large standard deviations and ranges. This group includes Cd, Zn, P, As, Sb, Pb, Sn, Cl, Ge, and Hg. The first group includes many of the elements with organic affinities and also those elements which are thought to be syngenetic and, therefore, inherited from an early period of coal swamp formation. The second group includes elements commonly found in coal, and in sedimentary rocks in general, as carbonates and sulfides. These minerals are often emplaced in coal by epigenetic mineralization.

Correlation coefficients for the various parameters determined for the coals from the Illinois Basin and for all of the 101 coals demonstrate the following geochemical associations:

1. The highest value for the correlation coefficients determined is that between Zn and Cd ($r = 0.93$). Both Zn and Cd are present in coals in the mineral sphalerite and probably essentially only in that form.

2. Elements commonly found in nature as sulfides are the chalcophile elements, which include As, Co, Cu, Ni, Pb, and Sb, which are all positively correlated with each other in the coals analyzed.

3. The lithophile elements, those commonly occurring in nature as silicates, include K, Ti, Al, and Si, which also have mutual positive correlations in the data reported. These elements are found in coals primarily as clay minerals (aluminosilicates).

4. Mn has a positive correlation of 0.63 with Ca in the coals analyzed, and does not correlate as well with any other parameter. It is present in small amounts and most likely is in solid solution with Ca in calcite ($CaCO_3$).

5. Sodium and Cl have a positive correlation of 0.53 in the coals studied.

Several additional geochemical relationships have been suggested by the chemical analytical data, such as:

a. The concentrations of As, Cu, Pb, Si, and Al in the coals of the Illinois Basin decrease from the older to the younger coals.

b. The correlation between Na and Cl increases from the older to the younger coals in the Illinois Basin.

c. The boron concentration in the coals of the Illinois Basin also increases from the older to the younger coals. This suggests that the Basin was becoming more marine (increasing in salinity) during the period of time between deposition of the older and the younger coals.

We expect that further interpretations of some of the relationships which have been noted and further elucidation of the geological parameters that have influenced the chemical characteristics of the coals will result from continued analyses of the data which are currently underway. These analyses will include areal mapping of concentrations of elements and also the mapping of the distributions of the elements within a single coal seam.

The average concentration of an element in the earth's crust is its clarke value. The mean value for each trace element was compared to the clarke for that element, and only three elements were enriched by at least one order of magnitude (present in an amount greater than 10 times the clarke) and three depleted by at least one order of magnitude (present in an amount less than one-tenth the clarke). Because of the large number of variables used in calculating various clarke values, differences of less than one order of magnitude were not considered significant. The three elements enriched in coals are Cd, Se, and B. Boron is concentrated only in the coals of the Illinois Basin and probably represents a higher salinity of the waters in the coal swamp or of the waters which flooded the coal swamp there. The only three elements found to be depleted are Mn, F, and P.

An analysis of the data from the laboratory-prepared (washed) coals has enabled the grouping of the determined elements, on the basis of their tendency to be concentrated with the cleanest coal or with the mineral matter. Those elements which are most closely associated with the clean coal are those with the highest "organic affinity" and include Ge, Be, and B. At the other end of the scale are those elements combined primarily in the mineral matter. This group has the least organic affinity and includes Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo. The remaining elements, which are apparently associated to varying degrees with both the organic and inorganic fractions of the coal, can be divided into two groups: those which are more nearly allied with the elements with organic affinities (P, Ga, Ti, Sb, and V) and those that generally are more inorganically combined (Co, Ni, Cr, Se, and Cu).

Many minerals have been reported from coals, including aluminosilicates, carbonates, and sulfides; and the mode of occurrence of the elements that make up those minerals is obvious. However, several additional elements were concentrated in some of the coals studied and the possibility that these elements too may be in discrete mineral phases was investigated.

Sphalerite (ZnS) has been identified as the host phase for both Zn and Cd in a number of coals, including all those which contained relatively high concentrations of Zn (greater than 500 ppm). The phosphate mineral apatite, more precisely a carbonate fluorapatite, was identified in the low-temperature ashes of both the coal sample that was found to contain the largest concentration of P and of the coal sample that contained the largest concentration of F.

A separate phase, identified as galena (PbS), has been observed in the low-temperature ash of a sample high in Pb. Both Ni and Cu have been identified in intimate association (probably in solid solution) with pyrite (FeS_2) in several samples.

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APPENDIX

PREPARATION OF COAL SAMPLES

Low-Temperature Ashing (LTA) and Trace Element Volatility

A coal ashing technique variously identified as electronic low-temperature ashing (LTA), radio-frequency ashing, or oxygen-plasma ashing was used to prepare samples in this study. Coal is ashed in commercially available devices (LFE Corporation Model LTA600 or the International Plasma Corporation Model 1101) in which oxygen is passed through a high-energy electromagnetic field produced by a radio-frequency oscillator. The oscillator tube operates at a frequency of 13.56 Mhz, in compliance with Federal Communications Commission requirements for scientific and medical equipment (Gleit, 1963). A discharge takes place, which produces an activated gas plasma consisting of a mixture of "atomic and ionic species as well as electronically and vibrationally excited states" (Gleit, 1963). As the activated oxygen passes over the coal sample, oxidation of the organic matter occurs at relatively low temperatures. The electronics involved is discussed in articles by the developers of this technique (Gleit, 1963; Gleit and Holland, 1962).

Coal for low-temperature ashing is ground to pass a 20-mesh sieve; approximately 50 g is placed in Pyrex boats, dried in a vacuum desiccator, and placed in the ashing chamber. Ashing takes place at a pressure of 1 to 3 torr at an oxygen flow rate of 50 to 100 ml per minute. The plasma temperature may be varied by changing the radio-frequency power level. At a radio-frequency power of 100 watts the plasma temperature is approximately 70° C. Higher temperatures are attained in the ashing chambers as a result of the exothermic oxidative reaction between the activated gases and the coal. Ashing temperature, monitored with a Raynger model LTX-28 infrared remote thermometer, was not allowed to exceed 150° C in this study. Prior to analysis, low-temperature ash samples are hand ground in an agate mortar and, depending on the analytical method used, dried at 110° C at atmospheric pressure or in a vacuum oven.

The effects of low-temperature ashing and of the oxidizing gas stream upon pure minerals and upon minerals in coal have been discussed in earlier papers (Gluskoter, 1965b, 1967; Rao and Gluskoter, 1973). No oxidation of minerals in the coal has been reported, and the only observed changes are those to be expected at a temperature of 150° C and pressure of 1 torr. Therefore, the major mineral constituents of coal—pyrite, kaolinite, illite, quartz, and calcite—are unaffected by radio-frequency ashing.

Most trace elements contained in coal mineral matter are not volatilized during low-temperature ashing; many elements thought to be present in organic combination are also retained in the low-temperature ash.

Samples prepared by low-temperature ashing have several important analytical advantages: (1) few trace elements are volatilized at the low ashing temperature (150° C); (2) no chemicals (such as are required for wet-ashing whole coal) need be added during preparation—only oxygen under a partial vacuum is introduced; (3) trace elements in the ash generally are concentrated by 10 or more times their amount in whole coal; and (4) subsequent analytical treatment is greatly simplified in most cases.

However, some of the more volatile trace elements, e.g., Hg, Br, F, and Sb, may be at least partially lost during low-temperature ashing. In testing for such elements, whole coal must be analyzed directly or combusted under controlled conditions.

Because conventional high-temperature ashing at 300° to 700° C in a muffle furnace may result in losses of Hg, Br, F, Se, Sb, As, and possibly other trace elements, low-temperature ashing in an oxygen atmosphere was investigated as a means of oxidizing coal organic matter without volatilization of trace elements. The volatility of each trace element during low-temperature plasma oxidation of coal was studied by one or more of the following procedures:

1) Volatile combustion products collected in cold-traps (-78° C) in the vacuum train of the low-temperature asher were analyzed.

2) Whole coal, which had been subjected to neutron irradiation, was ashed and any volatile radioisotopes collected in the cold-trap of the asher were determined and compared with their concentrations in the original sample.

3) Trace element results obtained from the direct analysis of whole coal were compared with results obtained from low-temperature and/or high-temperature ashes (700° C) prepared from the same coal to determine whether significant losses occurred during ashing. This procedure was also used to evaluate losses from coals ashed at 450° C.

The results of the foregoing tests show that only Hg (up to 90%), Br (100%), and Sb (up to 50%) are lost during low-temperature ashing of coal. Although F was not tested, it is presumed to be totally volatilized.

High-Temperature Coal Ash (HTA) and Trace Element Volatility

Analysis of low-temperature coal ash by optical emission spectroscopy has proved to be unsatisfactory because the ash contains various kinds of chemical compounds that behave erratically in the DC arc. High-temperature coal ash (450° to 500° C), which is composed of elemental oxides, is more amenable to analysis by optical emission. It is also more easily and rapidly prepared than low-temperature coal ash. Thus, high-temperature ash, prepared from -100 mesh coal, is used for both optical emission methods employed in this study. Care is used during the ashing procedure to oxidize all carbonaceous material. The coal ash is ground in an agate or mullite mortar and dried at 110° C prior to analysis.

To determine volatility losses, a set of samples from two coals was ashed in uncovered, used porcelain crucibles at temperatures of 300°, 400°, 500°, 600°, and 700° C. Trace element determinations were made on each of the 10 resulting ash samples. The analyses (tabl A) do not exhibit trace element losses or gains in samples ashed between 300° and 700° C except in C-16317, in which there was an apparent overall gain in boron concentration and a possible loss of lead at 300° C.

TABLE A—CONCENTRATIONS OF TRACE ELEMENTS IN MOISTURE-FREE COAL (ppm)
FROM HIGH-TEMPERATURE ASH SAMPLES PREPARED AT VARIOUS
TEMPERATURES IN USED PORCELAIN CRUCIBLES

	Sample number and temperature									
	C-16317					C-16030				
Element	300°C	400°C	500°C	600°C	700°C	300°C	400°C	500°C	600°C	700°C
Sn	4.4	< 4.2	< 4.2	< 4.2	< 4.2	< 2.0	< 2.0	< 2.0	< 1.9	< 1.9
B	62	90	104	119	106	23	31	34	46	40
Pb	77	61	64	65	64	43	49	46	4[illegible]	43
Cu	21	20	21	21	22	17	18	17	18	17
Co	7.9	-	8.5	8.9	8.4	15	19	17	17	19
Ni	39	39	36	39	35	44	47	47	47	49
Be	2.5	2.5	2.6	2.6	2.6	2.4	2.5	2.4	2.5	2.4
Cr	21	19	19	20	20	16	17	17	18	18
V	42	45	36	40	35	37	32	33	30	33
Mo	12	13	9.3	10	7.6	26	19	19	16	18
Ge	16	16	20	17	21	9.3	7.5	8.1	8.8	7.3

For both coals, the boron concentrations increased with ashing at temperatures from 300° to 600° C, and then decreased slightly between 600° and 700° C. Williams and Vlamis (1961) noted similar results when ashing plant material, with added $Ca(OH)_2$, in muffle furnaces, and when heating $Ca(OH)_2$ in the same furnaces in the absence of plant material. The increase in boron concentration was greater for samples in uncovered crucibles or dishes than for those in covered ones. Their explanation was that boron vapor from the walls of the muffle furnace condensed in the alkaline material. The concentration of boron increased with temperature and heating time.

To determine whether a similar change for boron takes place when ashing coal (without addition of alkaline material), we ashed two different coals in a Hoskins Electric Furnace, Type FD204A, in covered and uncovered platinum crucibles at 300°, 400°, 500°, 600°, and 700° C for 20 hours each. The results (table B) indicate that boron concentrations again showed an increasing trend when the coal was ashed in uncovered crucibles. However, in covered crucibles, the boron concentrations remain relatively constant until an ashing temperature of 700° C is reached. It should also be noted that the boron concentrations in the samples ashed in the covered crucibles are higher, in most cases, than in the corresponding uncovered samples. Apparently boron is lost from the samples in the uncovered crucibles more easily at lower temperatures, suggesting competing reactions, a loss mechanism, volatilization or retention on or in the crucible walls, and a reaction causing recombination of boron with the bulk sample. The recombination reaction becomes more efficient than the loss mechanism at higher temperatures in the uncovered crucibles. Loss of boron is prevented in the covered crucibles

TABLE B—ASHING TEMPERATURE STUDY WITH PLATINUM CRUCIBLES AND COVERS*

	Uncovered					Covered				
Element	300°C	400°C	500°C	600°C	700°C	300°C	400°C	500°C	600°C	700°C
						C-17601				
Sn	< 1.9	4.2	2.1	< 1.6	< 1.6	< 2.4	2.9	3.6	2.5	2.6
B	30	32	41	45	41	39	38	42	43	52
Cu	16	14	15	17	25	15	15	15	18	28
Co	15	15	13	14	13	14	14	14	13	13
Ni	39	38	36	37	35	39	37	37	36	35
Be	2.6	2.5	2.6	2.5	2.3	2.8	2.5	2.5	2.5	2.6
Cr	19	17	15	17	17	15	16	17	17	18
V	32	24	19	18	18	31	24	21	18	17
Mo	11	7.8	5.4	5.5	4.7	11	8.4	6.2	5.6	4.0
Ge	5.4	5.4	5.7	5.3	5.6	3.4	5.9	5.5	5.6	5.5
						C-17215				
Sn	7.4	7.0	6.8	7.4	8.0	8.4	7.0	6.7	5.9	7.3
B	48	53	64	64	70	78	65	77	72	93
Cu	16	17	18	29	33	22	17	17	20	34
Co	5.2	4.9	4.8	4.5	4.4	6.4	5.0	5.3	4.7	4.6
Ni	12	12	13	11	11	12	12	13	11	10
Be	5.4	5.5	5.4	5.3	5.6	6.6	5.5	6.0	5.3	5.6
Cr	23	22	22	20	20	23	21	21	21	22
V	44	36	33	28	28	48	37	34	27	26
Mo	7.2	6.2	5.3	4.2	4.0	9.8	6.4	6.4	4.7	3.7
Ge	14	16	14	16	18	18	14	17	15	16

* Same muffle furnace used throughout; concentrations - ppm; coal basis - moisture-free; ashing time - 20 hr, throughout.

when sufficient residence time is provided for the recombination reaction to occur. A reason for the apparent increase in boron concentration in the covered 700° C ash samples is not known.

The analytical data for copper indicate that some contamination may have resulted from the platinum crucibles, as seen from the similar concentration trends for covered and uncovered crucibles. Vanadium and molybdenum data indicated an apparent loss by volatilization during ashing as the temperature increased.

These increasing and decreasing concentration trends do not appear to be related to the spectrographic method used for analyses. Continuous time vs. relative intensity curves were obtained for the iron internal standard line and the boron, vanadium, and molybdenum analytical lines for sample C-17601 using the 300° and 700° C covered and uncovered ash samples. The resulting curves for each spectral line were similar regardless of the sample used, and in each case total line emission was attained within the 65 second exposure time normally used.

Although no carbonaceous material is visible, some residual organic material may remain in the coal ashed at 300° C. This may result in higher concentrations for some elements (V, Pb, Mo, etc.) because of the volatility of the organic species present. The observed differences in percent ash for LTA (150° C) and HTA (500° C) (see table 3) indicate that samples are not completely "ashed" at the lower temperature. (Approximately 1% carbonaceous material is normally present in LTA.) The data for Pb (table A) may be explained on this basis; however, results of the Mo and V determinations show a marked, continuous decrease in concentration up to 700° C. This is attributed to increased volatilization with increased temperature.

Evidence that the aforementioned losses of V and Pb may not be significant from a practical standpoint is shown by the general agreement of results obtained by optical emission, X-ray fluorescence, and atomic absorption for whole coal and low-temperature ash. The values for Mo are as yet unconfirmed.

The duration of the ashing period at 500° C in covered and uncovered platinum crucibles (table C) shows no appreciable influence, with the exception, previously noted, that there was the loss of boron from samples in uncovered crucibles, which reached a relatively constant concentration prior to five hours. Molybdenum and vanadium, which showed decreasing concentrations with increasing temperature, do not exhibit any ashing time dependence.

It is recommended that ashing be conducted in covered platinum or silica crucibles at 500° C if boron is among the elements to be determined. Further data concerning the concentration of boron determined in whole coal, when available, may require some changes in the coal ashing procedure used for this element. Uncovered crucibles may be used for ashing the samples for the other elements because small volatilization losses of vanadium and molybdenum are not prevented by covering the crucible during ashing.

Table D contains a summary of trace element volatilization losses for both high- and low-temperature ash. These results dictated the coal ashing

TABLE C—ASHING TIME VS. TRACE ELEMENT CONCENTRATIONS (ppm)

	C-17601*					
	Uncovered			Covered		
Element	5 hr	10.5 hr	20.75 hr	5 hr	10.5 hr	20.75 hr
Sn	1.8	2.1	< 1.6	< 1.7	< 1.7	< 1.7
B	39	38	35	47	42	44
Cu	16	18	16	17	16	17
Co	13	14	14	14	14	15
Ni	36	38	37	37	37	38
Be	2.4	2.5	2.8	2.4	2.5	2.8
Cr	17	19	19	17	17	19
V	20	19	21	22	21	19
Mo	6.2	5.9	6.0	7.5	6.5	6.4
Ge	5.0	5.6	5.5	6.0	6.3	6.0

* 500° C HTA, covered and uncovered Pt crucibles, same muffle furnace.

TABLE D—VOLATILITY OF TRACE ELEMENTS IN COAL

Low-temperature ash			High-temperature ash		
Retained (> 95%)		Lost	Retained*		Lost
Ga	Cu	Hg (up to 90%)	Zn	Cd	Mo**(33%)
Se	Pb**	Br (100%)	Ni	Mn	V**(possibly up to 25%)
As	V	Sb (up to 50%)	Co	Cr	
Zn	Mn	F (untested but presumed lost)	Cu	Be	
Ni	Cr		Pb**	Ge	
Co	Cd		B**	Sn	
Be				Se (untested but presumed retained)	

* No significant losses observed in coal ash from 300° to 700° C or between results from whole coal and low-temperature ash or high-temperature ash (~450° C).

** See discussion on high-temperature ash (p. 60-63).

method finally used for a particular trace element. Thus, determinations of Sb, Br, Hg, and F are performed on whole coal; Ga, Se, and As are determined in low-temperature coal ash; and the remaining elements may be determined in the more readily prepared high-temperature coal ash.

METHODS OF ANALYSIS

During the initial 12 months of this investigation, at least 10 chemists devoted many months to the development and application of analytical methods for the determination of trace, minor, and major elements in whole coal and coal ash. Existing procedures for coal or ash analysis, with only minor modifications, were found suitable for the analysis of many elements. However, the analysis of some elements required major changes or new approaches.

Initially, accuracy and precision of analysis were emphasized rather than speed. Where possible, results obtained from one method were critically compared with those of another, and refinements were made where necessary. The process was slow, and at the time of this writing, standards for the trace element composition of coal are not yet available. Round-robin testing for the standardization of multiple trace element concentrations in coal has been completed jointly by the U.S. Environmental Protection Agency and the National Bureau of Standards. The American Society for Testing and Materials, Committee D-5 on Coal and Coke, also has a new program for the standardization of methods for determining trace elements in coal. The Illinois State Geological Survey has been active in both studies.

In this investigation, six independent instrumental methods were used to analyze whole coal and coal ash. Considerable overlap occurs in the elements determined by each method. As the investigation progressed, the procedures that proved most precise, accurate, and convenient were used for routine analysis.

The analytical methods were developed by the following personnel in the Survey's Analytical Chemistry Section: X-ray fluorescence (X-RF) by John K. Kuhn, atomic absorption (AA) by Peter C. Lindahl, optical emission-direct reading (OE-DR) by Gary B. Dreher, optical emission-photographic (OE-P) by John A. Schleicher, neutron activation analysis (NAA) by Joyce Kennedy Frost, Patricia M. Santoliquido, and R. R. Ruch, and ion-selective electrode (ISE) by Josephus Thomas, Jr.

X-Ray Fluorescence Analysis of Whole Coal and Coal Ash

X-ray fluorescence determinations were made on whole coal for As, Br, Pb, Zn, Cu, Ni, P, Cl, S, V, Mg, K, Ca, Fe, Ti, Al, Si, Mn, Co, and Cr and on coal ash for Ni, P, V, Mg, K, Ca, Fe, Ti, Al, and Si. A Philips vacuum spectrometer equipped with a Mark I solid-state electronic panel was used for all analyses.

A chromium target X-ray tube was employed for the determination of all elements except Co, Cr, and Mn; for these, a tungsten target X-ray tube was used. Additional elements might also be determined by using equipment of more advanced design than was available for this study. Goniometer and other

TABLE E—X-RAY FLUORESCENCE SETTINGS FOR THE ANALYSIS OF COAL AND COAL ASH

						Pulse height analyzer	
Element	X-ray	2θ angle	Background 2θ	Crystal	Vacuum	Base	Window
Si	KL_3 & KL_2	108.01	111.01	EDDT	yes	7	17
Al	KL_3 & KL_2	142.44	145.95	EDDT	yes	5	12
Ti	KL_3 & KL_2	86.12	89.12	LiF	no	5	18
Fe	KL_3 & KL_2	57.51	60.51	LiF	no	5	25
Ca	KL_3	44.85	47.95	EDDT	yes	14	30
K	KL_3 & KL_2	50.32	53.90	EDDT	yes	14	21
Mg	KL_{23}	136.69	139.69	ADP	yes	4	8
V	KL_3 & KL_2	76.93	80.93	LiF	no	5	16
S	KL_3 & KL_2	75.24	78.38	EDDT	yes	12	18
Cl	KL_3	64.94	67.94	EDDT	yes	11	19
P	KL_3 & KL_2	110.99	113.99	Ge	yes	9	15
Ni	KL_3 & KL_2	48.66	50.36	LiF	yes	10	27
Cu	KL_3 & KL_2	45.02	49.67	LiF	yes	11	28
Zn	XL_3 & KL_2	41.79	44.25	LiF	yes	10	22
Pb	L_3N_5 & L_2M_4	28.24	31.24	LiF	yes	22	28
Br	KL_3 & KL_2	29.97	35.12	LiF	yes	25	23
As	KL_3 & KL_2	34.00	37.00	LiF	yes	24	23
Co	KL_3 & KL_2	52.79	55.79	LiF	yes	8	40
Cr	KL_3 & KL_2	69.35	72.35	LiF	yes	6	28
Mn	KM_{23}	56.64	59.64	LiF	yes	8	25

instrument settings used for the analyses are listed in table E. The sample preparation procedure follows.

Low- and High-Temperature Coal Ashes

Coal ash is composed entirely of inorganic mineral matter; whole coal is composed primarily of organic compounds containing carbon, hydrogen, oxygen, nitrogen, and sulfur, with only minor amounts of mineral matter. Because of the large and variable percentages of relatively heavy elements in both low- and high-temperature coal ashes, matrix-related problems are troublesome and, for the determination of major and minor elements, can best be overcome by use of a dilution technique such as that described by Rose, Adler, and Flanagan (1962) and used extensively for geological samples. For this procedure, low-temperature ash is dried in a vacuum oven, and high-temperature ash is dried at 105° C in air. Ashes must be stored in a desiccator because many absorb relatively large quantities of water in a few minutes. From the dried sample, 125 mg is weighed into a graphite crucible containing 1.0000 g of lithium tetraborate. The sample is placed in a depression made in the tetraborate, thereby preventing sample contact with the crucible wall. Next, 125 mg of lanthanum oxide is added as a heavy-element X-ray absorber, and the contents of the crucible are mixed with a glass rod as thoroughly as possible without scraping the crucible wall or bottom. This mixture is fused in a furnace for 15 minutes at 1000° C, removed, covered with a second crucible, and allowed to cool to room temperature. The resulting fused pellet is then weighed to determine fusion loss and placed in the grinding vial of a No. 6 "Wig-L-Bug" grinder with 2 percent by weight of Somar mix (a commercial mixture used as a grinding and plasticizing agent). The sample is ground for 3 minutes, transferred to a 1 1/8-inch die, and pressed at 40,000 psi. Samples are placed in the spectrometer and exposed to the X-rays, and the various elements are determined in the usual fashion. When backed with an appropriate material, the pressed disk is at least semipermanent.

For calibration, each sample is compared to a group of analyzed standards with a range of major and minor element concentrations similar to the ranges of the unknown coal ash samples. The U.S. Geological Survey standard silicate rock samples are convenient for this purpose.

Whole Coal

Coal is a heterogeneous mixture of organic compounds composed of relatively light elements (H, C, N, O, S). Of the inorganic constituents, pyrite (iron and sulfur) exhibits considerable variation, rarely falling short of 0.2 percent or exceeding 5.0 percent of bituminous and higher rank coals. Concentration ranges of other major elements are less. Consequently, absorption and enhancement effects are minimal, and the absorption characteristics of the sample matrix are relatively constant. Effects due to matrix variations are generally small and corrections for them are easily made.

To prepare the whole coal disk for X-ray fluorescence analysis, 2.0000 g of air-dried coal is placed in the grinding vial of a No. 6 "Wig-L-Bug" grinder along with 10 percent by weight of Somar mix. The mixture is ground for 3 minutes, transferred to a die and, with a suitable backing, pressed into a disk at a pressure of 40,000 psi. The disk is dried in vacuum to prevent losses that could occur at higher temperatures in a drying oven. Determinations of all major, minor, and trace elements except iron, titanium, and vanadium are performed in vacuum to avoid X-ray scattering due to adsorption of water on the surface of the whole coal disk.

Standards are prepared from analyzed coals by the same procedure, and all determinations are made in order of descending potential volatility. Some absorption-enhancement effects, primarily from iron, do occur and must be dealt with individually for each trace element affected. One method for making such corrections is to observe the effect of adding different amounts of iron to a coal of known composition on the count rate for each element and to make appropriate adjustments.

The concentration of an element in a sample of unknown composition is calculated by using a concentration/count "factor," which is the ratio of the concentration of the element in chemically analyzed standards to the background-corrected count rate for a given element (see table E for 2θ angular settings). This ratio is defined by the slope of the calibration curve obtained from a plot of the count rate for each element in the standards vs. the element's respective concentration. The concentration of any element in a sample being analyzed is the product of its "factor" multiplied by the count rate.

Effect of Whole Coal Particle Size on Precision

A set of nine whole coal samples was analyzed by X-ray fluorescence to determine the effect of particle size upon the precision of measurement. Representative portions of each coal were sequentially ground to pass through 60, 100, 200, 325, and 400 mesh sieves. Duplicate 2-gram samples from each mesh size were weighed and further reduced in size by grinding for 3 minutes in a No. 6 Wig-L-Bug. The final grinding eliminated, as nearly as possible, any size segregation in the pressed coal disks. The disks were subsequently prepared for analysis as previously described.

Table F shows the differences in concentrations, expressed in percentage or parts per million, between duplicate coal samples. Progressive reduction of coal particle size from -60 to -400 mesh resulted in better agreement between duplicate coal samples for all trace elements determined except Br. Most notable improvements observed were for Ni, Cu, Zn, and Pb. In all cases, the mean of the relative differences between duplicate determinations was reduced below 5 percent for coal ground to pass -200 mesh size.

The data given in table G demonstrate that for most purposes acceptable precision can be obtained on -200 mesh coal, but not on -60 mesh coal. Further improvement in precision may be obtained by grinding coal samples to pass a -325 mesh screen, but such a high degree of precision is not generally necessary except for special purpose analyses, e.g., for making standard samples. Variation in the initial coal sampling procedure would probably negate any small improvement in precision which might result from further grinding.

These conclusions are based on nine coal samples and hundreds of individual analyses and therefore represent a reasonably good statistical base.

While the accuracy of X-ray fluorescence methods for the analysis of whole coal may suffer somewhat from lack of good standards, the precision is at least as good as in other methods used in this study. Consequently, it is felt that the conclusions reached are valid for any method using a 1- or 2-gram sample for analysis.

Comparative Analyses

Table H compares the mean values for coal ash analyses made by X-ray fluorescence at the Survey with those made by the British Coal Utilization Research Association (Dixon et al., 1964). The latter samples were analyzed in many laboratories by a variety of wet chemical and instrumental methods. Results show the X-ray method to be accurate for the oxides listed. Additional comparisons given for 25 coals (Ruch, Gluskoter, and Shimp, 1973) show that whole coal X-ray fluorescence determinations of As, Br, V, Cu, Ni, Zn, and Pb are in good agreement with results of coal ash analyses obtained by the other independent methods used in that study. Further, results of X-ray fluorescence analyses of whole coal for Si, Al, Ca, Mg, Fe, K, Ti, and P compare favorably with fluorescent analyses of coal ash prepared from the same coals when results are converted to a whole coal basis from the percentage of ash in the coal.

TABLE F—DIFFERENCES BETWEEN DUPLICATE ANALYSES OF WHOLE COAL SIZE FRACTIONS

Element	-60 mesh	-100 mesh	-200 mesh	-325 mesh	-400 mesh	Extra-fine mesh	Concentration unit
Fe	0.03	0.01	0.00	0.01	0.01	0.00	%
V	1.3	2.9	1.7	2.4	0.6	0.4	ppm
Ti	0.01	0.01	0.02	0.02	0.01	0.01	%
Al	0.03	0.08	0.03	0.02	0.04	0.01	%
Si	0.07	0.01	0.05	0.01	0.02	0.03	%
K	0.004	0.003	0.005	0.002	0.002	0.001	%
Ca	0.015	0.017	0.023	0.018	0.005	0.004	%
S	0.02	0.02	0.02	0.01	0.00	0.02	%
Cl	0.001	0.003	0.002	0.004	0.001	0.003	%
P	1.3	1.6	2.1	1.3	1.0	1.0	ppm
Mg	0.012	0.012	0.010	0.011	0.005	0.005	%
Ni	1.9	1.7	3.2	2.9	0.9	0.8	ppm
Cu	4.8	0.8	0.2	0.1	0.1	0.1	ppm
Zn	8.5	1.0	0.5	1.3	0.2	0.2	ppm
Pb	2.8	1.9	2.0	0.4	0.8	0.9	ppm
As	3.0	1.4	1.9	0.0	0.3	0.6	ppm
Br	0.8	0.4	0.5	0.4	0.3	0.2	ppm

TABLE G—RANGE OF RELATIVE DIFFERENCES (%) BETWEEN DUPLICATE ANALYSES FOR EACH TRACE ELEMENT AT THREE COAL MESH SIZES

Element	-60 mesh	-200 mesh	-325 mesh
V	0.0 - 10.0	0.3 - 5.0	0.3 - 4.0
P	2.0 - 18.0	2.0 - 10.0	1.5 - 7.5
Ni	1.5 - 25.0	0.0 - 20.0	1.5 - 8.0
Cu	0.8 - 20.0	0.2 - 1.0	0.2 - 1.0
Zn	1.2 - 25.0	1.2 - 12.0	0.1 - 6.5
Pb	0.4 - 23.0	1.2 - 9.5	0.4 - 5.0
As	0.1 - 6.0	0.1 - 4.0	0.0 - 1.5
Br	0.0 - 4.0	0.0 - 3.5	0.0 - 3.0

TABLE H—COMPARISON OF ISGS X-RAY FLUORESCENCE ANALYSES OF COAL ASH WITH BCURA* ANALYSES (in percent)

	BCURA No. 4		BCURA No. 5		BCURA No. 7		BCURA No. 10		BCURA Slag		
Oxide	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	Ave. diff.
SiO_2	53.28	53.41	29.27	29.43	20.01	20.37	44.03	44.49	51.45	51.58	0.25
TiO_2	1.65	1.70	0.65	0.70	0.26	0.34	1.18	1.19	0.96	0.96	0.04
Al_2O_3	34.11	33.88	19.73	19.82	10.03	10.33	29.93	30.02	28.20	28.45	0.19
Fe_2O_3	5.83	5.76	39.02	39.24	62.16	62.31	13.56	13.82	6.27	5.99	0.17
MgO	0.66	0.71	1.18	1.29	0.58	0.63	2.05	2.00	2.33	2.26	0.06
CaO	0.73	0.77	2.47	2.54	2.31	2.30	1.24	1.29	7.89	7.91	0.04
K_2O	2.45	2.38	1.94	1.95	1.38	1.39	3.68	3.71	2.84	2.81	0.03
P_2O_5	0.48	0.41	0.14	0.14	0.17	0.15	0.77	0.77	0.09	0.05	0.03

* British Coal Utilization Research Association (Dixon et al., 1964).

Because analyses performed by the optical emission and atomic absorption methods used in this study are made on high- and low-temperature ashes, small variations from the results obtained on whole coal samples by X-ray fluorescence are to be expected. For Zn and As, variations are larger at high concentrations. At least some of this variation is due to differences in sample particle size and the occurrence of discrete mineral particles in whole coal.

Precision

Relative standard deviation (1 σ) for X-ray fluorescence analyses of whole coal in this study are as follows: Si - 0.35 percent, Ti - 1.9 percent, Al - 0.9 percent, Fe - 1.2 percent, Mg - 3.3 percent, Ca - 0.1 percent, K - 0.7 percent, P - 1.6 percent, V - 1.3 percent, S - 0.5 percent, Cl - 4.2 percent, Ni - 8.4 percent, Cu - 4.0 percent, Zn - 3.8 percent, Pb - 1.9 percent, As - 1.8 percent, and Br - 2.0 percent.

Optical Emission Spectrometric Analysis of High-Temperature Coal Ash

Trace quantities of 11 elements in high-temperature coal ash samples containing 10 to 30 percent Fe as Fe_2O_3 were determined simultaneously and rapidly with a Jarrell-Ash Model 750 direct-reading emission spectrometer, using Fe (2483.27 Å) as a variable internal standard. As little as 20 mg of coal ash sample sufficed for quadruplicate analyses. The elements determined by this method in this study are B, Pb, Cu, Co, Ni, Be, Cr, V, Sn, Mo, and Ge.

Construction of Calibration Curves

Eight standard samples were prepared by adding various amounts of a synthetic standard (1000 ppm of each of the elements to be determined) to U.S. Geological Survey standard granite G-2 (adjusted to a SiO_2:Al_2O_3 ratio of 3:1 by addition of 379 mg of spectroscopically pure Al_2O_3 to 0.50000 g of G-2).

TABLE I—CONCENTRATIONS IN STANDARD MATERIALS OF G-2 BASE IN 3:1 SiO_2-Al_2O_3 MATRIX + 1000 ppm SYNTHETIC STANDARD FOR SPECTROMETRIC METHOD

Element	Weight of synthetic standard (mg) added to 0.5 g G-2 + 379 mg Al_2O_3								Weight of $Na_2B_4O_7 \cdot 10H_2O$ (mg)
	0.00	1.00	4.04	9.19	19.79	54.45	133.22	535.89	6.32
	Parts per million								
B	1.86	2.84	5.78	10.7	20.5	50.2	106	264	1320
Pb	26.7	28.5	33.9	43.0	61.2	116	220	512	
Cu	9.95	11.8	17.3	26.6	45.1	101	206	504	
Co	4.55	6.40	12.0	21.3	39.9	96.0	202	501	
Ni	5.95	7.79	13.4	22.6	41.2	97.3	203	502	
Be	2.23	4.08	9.67	19.0	37.6	94.0	200	500	
Cr	8.37	10.2	15.8	25.0	43.6	99.5	205	503	
V	34.4	36.2	41.6	50.6	68.7	123	226	516	
Sn	0.93	2.78	8.37	17.7	36.4	92.8	199	500	
Mo	1.12	2.97	8.57	17.9	36.6	92.9	199	500	
Ge	0.66	2.51	8.11	17.5	36.1	92.5	199	499	

The preparation and resulting concentrations are summarized in Table I. A ninth standard sample composed of 0.50000 g of G-2, 379 mg of Al_2O_3, and 6.32 mg of $Na_2B_4O_7 \cdot 10H_2O$ was later prepared to increase the range of the boron calibration curve to 1320 ppm.

The final mixtures for all standard and coal ash samples include 40 mg of standard or coal ash, 10 mg of spectroscopically pure $Ba(NO_3)_2$, and 150 mg of SP-2X graphite powder. They are combined by mixing in a plastic vial half an inch in diameter by 1 inch high that contains two plastic balls an eighth of an inch in diameter. One mixture is prepared for each of the nine standards. The small amount of $Ba(NO_3)_2$ is added to improve the arcing characteristics and the reproducibility of results from replicate analyses. Higher amounts of $Ba(NO_3)_2$ (up to 120 mg in 200 mg total mixture, 40 mg of sample) decreased reproducibility.

The effect of varying concentrations of Fe_2O_3 in the standards was investigated; relative intensities of analytical lines were not found to be dependent upon the iron concentration, except in the cases of weak spectral interference.

Internal Standardization

Because an iron line was used as the variable internal standard, the concentration of iron in each coal ash sample was determined by X-ray fluorescence analysis of the whole coal. A response curve for the Fe 2483.27 Å internal standard line was drawn. Six coal ash samples with known different Fe_2O_3 concentrations were arced under identical conditions, and the relative intensity values of the Fe internal standard line were plotted versus Fe_2O_3 concentration on log-log graph paper. The standardized relative intensity shown on this response curve for Fe 2483 Å was used to preset the spectrometer for each sample arced.

Standard Conditions

The sample electrode (anode) is a thin-walled crater electrode with an outside diameter of one-eighth of an inch and a crater one-fourth of an inch deep (National L-3979 or equivalent). The cathode is a pointed counter electrode one-eighth of an inch in diameter (National L-4036 or equivalent). The analytical gap of 6 mm is surrounded by a 10 SCFH flow of gas composed of 80 percent argon and 20 percent oxygen. A short-circuit current of 15 amperes DC is maintained for 65 seconds while arcing a sample charge of 15 mg. The proportions in the sample mixture are 4:1:15 [sample:$Ba(NO_3)_2$: graphite powder] for standard and coal ash samples.

The wavelengths of the analytical lines used are listed in table J.

TABLE J—ANALYTICAL WAVELENGTHS AND RELATIVE STANDARD DEVIATIONS FOR THE DETERMINATION OF TRACE ELEMENTS IN HIGH-TEMPERATURE COAL ASH BY DIRECT READING SPECTROMETRY

Element	Analytical wavelength (Å)	Average relative standard deviation (%)	Range of relative standard deviation (%)
B	2496.8 (second order)	5.2	1.0 - 13
Pb	2833.07	8.6	3.8 - 14
Cu	3273.96	7.5	2.9 - 20
Co	3453.50	4.8	1.1 - 19
Ni	3414.76	4.7	2.4 - 11.2
Be	2348.61	3.6	1.2 - 8.6
Cr	4254.35	4.0	1.0 - 9.1
V	3185.40	6.6	2.8 - 11
Sn	3034.12	22	10 - 73
Mo	3170.35	6.3	2.6 - 22
Ge	2651.18	16	3.0 - 42

Comparative Analyses

Results for V, Be, Cu, Ni, Pb, Ge, Cr, B, and Co, calculated to a whole coal basis, have been shown by Ruch, Gluskoter, and Shimp (1973) to be in good agreement with those obtained by atomic absorption spectrometry (LTA), X-ray fluorescence spectrometry (whole coal), photographic optical emission spectroscopy (HTA), and neutron activation (NAA).

Table J lists the average relative standard deviations and their ranges for each element. Most of the coal ash samples contain Sn in concentrations less than the detection limit, making the precision values for Sn meaningless. Because the analytical line for Ge is weak, a small change in the number of Ge atoms emitting at that wavelength in the arc during the arcing period produces a relatively large change in line intensity.

Optical Emission Spectrographic Analysis of High-Temperature Coal Ash

Samples of coal ash ignited to 500° C were analyzed by the photographic method of emission spectrography with a Jarrell-Ash 3.4 m Ebert grating spectrograph. The elements so determined are: B, Mn, Cr, Ge, Pb, Be, Mo, V, Cu, Zn, Zr, Co, and Ni. Analyses of Ag and Bi were attempted, but their concentrations were below the respective detection limits.

Construction of Calibration Curves

Because of the high concentrations of many trace elements in coal ash and the inability of the photographic plate to record accurately the large amount of light emitted, a 6 percent neutral density filter is inserted in the light path of the spectrograph to attenuate the emitted light. Synthetic standards containing 1, 10, 50, 100, 250, 500, and 1000 ppm of the elements to be determined are prepared (from commercially available mixtures) in a base matrix having a 3:1 silica-to-alumina ratio. To these standards is added 10 percent Fe_2O_3, so that the final concentration of elements to be determined is 0.9, 9, 45, 90, 225, 450, and 910 ppm.

The first two standards are generally too low in concentration to be measured; consequently, 10 mg of the higher concentration standards are mixed in replicate with 10 mg of graphite and arced to completion plus 10 seconds (about 150 seconds). The transmissions of the attenuated lines, as recorded on an 8 by 10 inch Eastman Spectrum Analysis No. 1 photographic plate, are measured on a densitometer-comparator, and the values are converted to their Seidel transformed values.

Seidel values are plotted against concentration on semi-log paper and the resultant curves transferred to a calculating board. After attenuation of light from the arc, background on the photographic plate is barely dense enough to overcome emulsion inertia; therefore no corrections are made.

Standard Conditions

The sample electrode (anode) used is graphite; the counterelectrode is one-eighth-inch tapered graphite rods rounded to a radius of one-thirty-second of an inch at the tip. Current used is 11 amperes true at 220 volts. The electrode spacing is 4 mm, and the analytical gap is surrounded by a 14 SCFH laminar flow of 80 percent argon and 20 percent oxygen. Photographic plates are developed in Eastman D-19 developer for 3.0 minutes, shortstopped in 11 percent acetic acid for 30 seconds, and fixed for 4 minutes in Eastman Fixer. Plates are then washed in running tap water for 20 minutes, rinsed in deionized water, and dried. Wavelengths of analytical lines used are given in table K.

TABLE K—ANALYTICAL WAVELENGTHS AND RELATIVE STANDARD DEVIATIONS FOR THE DETERMINATION OF TRACE ELEMENTS IN HIGH-TEMPERATURE COAL ASH BY PHOTOGRAPHIC OPTICAL EMISSION

Element	Analytical wavelength (Å)	Relative standard deviation (%)
B	2497.7	12
Mn	2576.1	19
Cr	2677.2	23
Ge	2651.2	16
Pb	2833.1	9
Bi	3067.7	--
Be	3130.4	14
Mo	3170.4	22
V	3184.0	30
Cu	3247.5	18
Ag	3280.7	--
Zn	3345.0	--
Zr	3392.0	37
Co	3405.1	25
Ni	3414.8	24

In a number of coal ash samples an extremely faint Ag line was observed, but the amount present was too small to be accurately measured. In addition, many ashes contained high Zn concentrations outside the analysis limitations of this photographic method.

Comparative Analyses

Although the precision values (table K) indicate a relatively high error for the method, averages of replications for V, Be, Cu, Ni, Pb, Ge, Cr, Co, and Zn show generally good agreement with other methods of analysis when all values are calculated to the whole coal basis (Ruch, Gluskoter, and Shimp, 1973). This agreement is particularly true for concentrations in the lower ranges—25 ppm or less. However, at or near 100 ppm, agreement with other methods is poor.

Atomic Absorption Analysis of Coal Ash

An atomic absorption method for the determination of Cd, Cu, Ni, Pb, and Zn in ash from coal and coal float-sink fractions has been extensively investigated. Both the low- and high-temperature coal ash and the low-temperature ash from coal float-sink fractions can be readily analyzed by atomic absorption spectrophotometry when an acid digestion bomb is used for sample treatment.

The digestion bomb technique for the decomposition of silicates (Bernas, 1968; Langmuhr and Paus, 1968) and aluminosilicates (Buckley and Cranston, 1971) was modified and found applicable to the decomposition of ashed samples of coal and coal float-sink fractions.

Atomic absorption measurements were made using a Beckman Model 1301 Atomic Absorption Accessory with a Beckman DB-G Grating Spectrophotometer. Measurements were recorded on a Beckman Model 1005 Linear-Log Ten-Inch Potentiometric Recorder, which was coupled with a Beckman 73490 Scale Expander. A Beckman 100410 Autolam Burner was used with an air-acetylene flame. Standard single-element hollow cathode lamps were used. Corrections for background absorption were made using a non-absorbing spectral line from either a hydrogen-continuum source or a hollow-cathode lamp.

Reagents and Construction of Calibration Curves

All reagents used are ACS certified reagent grade chemicals, and standard stock solutions are prepared from high-purity metals. A standard stock solution of each element—Cd, Cu, Ni, Pb, and Zn—is prepared to give a metal ion concentration of 100 ppm. Calibration standards prepared from diluted stock solutions containing 1.4 percent aqua regia, 1 percent HF, and 1 percent H_3PO_3 are made up so that the standards match the sample solutions obtained in the decomposition method.

Sample Decomposition Procedure

The decomposition of the low-temperature ash of coal, the float-sink fractions of coal, and the high-temperature coal ash is carried out in a Parr 4745 acid digestion bomb.

Approximately 0.1 g of the ashed coal material—previously ground in an agate or mullite mortar and dried at 110° C for several hours—is transferred to the Teflon cup of the decomposition vessel. The low-temperature ash sample is treated with 1.0 ml of concentrated HCl and then heated to dryness on a steam table. The HCl treatment is omitted for high-temperature ash samples. Both types of samples are then wetted with 0.7 ml of aqua regia (1:3:1 HNO_3-HCl-H_2O), 0.5 ml of HF is added, and the acid digestion bomb is closed. The bomb is heated at 100° to 110° C for 2 hours. After it cools to ambient temperature, the bomb is disassembled and the decomposed sample treated with 10 ml of a H_3BO_3 solution (0.05 g per ml) to complex the fluorine. The dissolved sample is transferred to a 50 ml Pyrex volumetric flask, diluted to volume with deionized water, and placed in a polyethylene bottle for storage.

Atomic Absorption Spectrophotometric Procedure

The following analytical wavelengths are used: 228.8 nm (Cd), 324.7 nm (Cu), 232.0 nm (Ni), 283.3 nm (Pb), and 213.9 nm (Zn). Samples analyzed for Cd, Ni, Pb, and Zn are reaspirated at a nearby nonabsorbing hollow-cathode lamp spectral line or at the analytical line using a hydrogen continuum source for background correction. Cation standards are prepared with the following indicated ranges: 0.1 to 1.0 ppm for Cu, Ni, and Zn; 0.1 to 5.0 ppm for Pb; and 0.01 to 0.5 ppm for Cd. In determinations of all elements except Zn, the sample being analyzed requires no further dilution; for Zn an additional dilution might be necessary. Metal ion concentrations in the samples are calculated by interpolation from a calibration curve of absorbance vs. concentration. A new calibration curve is constructed for each set of analyses.

Comparative Analyses

Results obtained by atomic absorption spectrophotometry for Cd, Cu, Pb, and Ni concentrations, expressed on the whole coal basis, agree well with results obtained by the other analytical methods used in this study; and atomic absorption results for low- and high-temperature ashes prepared from the same coal sample also compared well when expressed on the whole coal basis (Ruch, Gluskoter, and Shimp, 1973). These favorable comparisons indicate that these trace elements are not volatilized when coal is ashed at 450° to 500° C.

The determination of Zn in the coals and coal ashes studied presented a unique sampling problem. In a few samples, marked variations in Zn results were observed. The Zn content of these coals is attributed primarily to the presence of discrete particles of sphalerite (ZnS), which contributes to the inhomogeneity of a coal sample and thus can result in significant variations in Zn concentrations. The degree of coal grinding required to achieve representative samples is being studied further. Decreasing the particle size prior to the reduction in sample quantity should improve agreement among the various methods of analysis.

Estimates of the average relative standard deviation for elements determined by atomic absorption spectrophotometry are 10 percent or better.

Neutron Activation

Radiochemical separations performed on low-temperature coal ash are used for the determination of Se, As, Ga, Zn, and Cd. Whole coal is used for the determination of Hg, Sb, and Br, which are totally or partially volatilized during low-temperature coal oxidation. Manganese and Na are determined by instrumental neutron activation analysis. Float-sink fractions of the coal samples are processed in the same manner as coal samples.

All irradiations are made in the University of Illinois Advanced TRIGA reactor, utilizing a thermal neutron flux of 1.4×10^{12} neutrons cm^{-2} sec^{-1}. During irradiation the samples and standards are rotated at 1 rpm to insure equal neutron flux.

The containers used for the samples and standards in the irradiations are two-fifths-dram polyethylene snap-cap vials previously cleaned with deionized water and acetone.

The γ-ray counting system consisted of a 3 inch by 3 inch NaI(Tl) detector connected to a Nuclear-Chicago 400-channel analyzer.

Chemical yields are obtained for each sample to determine losses during radiochemical separations.

Determination of Se in Low-Temperature Coal Ash

Each sample (about 200 mg) of low-temperature coal ash is accurately weighed into a polyethylene vial. The samples and a sealed polyethylene vial containing a comparative standard of 1 mg Se per ml solution (prepared by dissolving spectrograde Se metal in HNO_3 and HCl) are irradiated for 2 or 3 hours, and then allowed to decay for 3 days.

Each sample is quantitatively transferred to a 100-cc round-bottomed distillation flask, and then 20 ml of concentrated HCl, 5 ml of concentrated HNO_3, 5 ml of concentrated $HClO_4$, and 3 ml of Se carrier (containing 10 mg Se per ml) are added. This mixture is refluxed overnight.

The mixture is distilled to a volume of about 10 ml in an air stream, and the distillate collected in 2 ml of distilled water in a flask in an ice bath. Ten ml of concentrated HCl and 12 ml of concentrated HBr are added to the distilling flask and distilled. Second portions of HCl and HBr are added and the distillation is repeated. To the combined distillate, 7 ml of 6 percent sulfurous acid (H_2SO_3) is added to precipitate red amorphous Se, which is allowed to settle.

The supernatant liquid is decanted through a Teflon-coated filtering apparatus containing a weighed filter paper. Hot water is added to the Se in the beaker to convert it to gray metallic Se, which is filtered, washed with more hot water and acetone, air-dried for 2 hours, weighed, and then mounted on cardboard.

The Se comparative standard is diluted 1:100 with water, and 1 ml (10 µg of Se) is transferred to a flask containing 3 ml of Se carrier. The standard is distilled and precipitated in the same manner as the samples. Radiochemical yields of the samples and standard are quantitative.

Samples and standard are counted for the activity of the 0.121 and 0.136 MeV gamma rays of ^{75}Se, which has a half life of 120 days. These two gamma rays give a single photopeak with the 3 inch by 3 inch NaI(Tl) detector and 400-channel analyzer.

The Se concentration of the low-temperature coal ash samples is calculated and, by using the percentage of low-temperature ash in the coal, converted to ppm of Se in whole coal. The relative standard deviation of a measurement is normally better than 10 percent. Analysis of the National Bureau of Standards (NBS) SRM-1630 for Se gave the result 2.0 ± 0.13 ppm, which compares favorably with the provisional value of 2.1 ppm established by the NBS.

Determination of As in Low-Temperature Ash

Each sample (about 200 mg) of low-temperature coal ash is accurately weighed into a two-fifths-dram polyethylene vial. The samples and a sealed polyethylene vial containing a comparative standard of 10 mg As per ml (prepared by dissolving sodium arsenite [$NaAsO_2$] in water and H_2O_2) are irradiated for 2 hours and allowed to decay overnight.

Each sample is quantitatively transferred to a 100-cc round-bottomed distillation flask; and 20 ml of concentrated HCl, 5 ml of concentrated HNO_3, 5 ml of concentrated $HClO_4$, and 3 ml of As carrier solution (10 mg As per ml) are added. The mixture is refluxed overnight and distilled to a 10-ml volume in an air stream; the distillate is collected in 30 ml of distilled water. Ten ml of concentrated HCl and 12 ml of concentrated HBr are added to the distillation flask, and this mixture is distilled. Second portions of HCl and HBr are added, and the distillation is repeated. Five g of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) are added to the combined distillate, and the mixture is heated to just below the boiling point for 2 to 3 hours until the solution clears and the black As metal precipitate is completely digested. The As precipitate is suction-filtered onto a weighed filter paper, washed with distilled water and acetone, air-dried, weighed, and mounted on cardboard.

The As standard is diluted 1:250 with dilute HCl and a 1-ml aliquot (40 g of As) is transferred to a flask containing 3 ml of As carrier. The standard is distilled and precipitated in the same manner as the samples. Radiochemical yields of the sample and standard are quantitative.

The samples and standard are counted for the activity of the 0.559 MeV γ-ray photopeak of 26.5 hr ^{76}As.

The As concentration of the low-temperature coal ash samples is calculated and converted to ppm As in whole coal from the percentage of low-temperature ash in the coal. The maximum relative standard deviation of a measurement is 12 percent.

Radiochemical Separation and Determination of As in Coal with an Inorganic Exchanger (Acid Aluminum Oxide)

A carrier-free separation of arsenic by retention on acid aluminum oxide (AAO) ion exchange columns is a second neutron activation method developed for the analysis of coal ash.

One hundred mg of an irradiated low-temperature ash sample, using the same sample preparation and irradiation procedure as previously described for As, is fused with 2 g NaOH. The melt is dissolved in 10 ml of distilled water, and 14 ml of concentrated HNO_3 is added. The resultant solution, which is ~7M HNO_3, is passed through a chromatographic column (7 mm by 40 mm) filled with acid aluminum oxide (1.6 g) and then the column is rinsed with 10 ml of 7M HNO_3. Arsenic-76 retained on the column is counted. The standard solution (17 µg As in 0.5 ml) is taken up in 25 ml of 7M HNO_3, passed through and retained on an acid aluminum oxide column, and then counted. The loading capacity of the exchanger is 43.5 µg As/g AAO.

Results of triplicate As determinations for the two neutron activation methods are in excellent agreement (table L).

TABLE L—COMPARISON OF MEAN ARSENIC VALUES OBTAINED BY INORGANIC EXCHANGER AND DISTILLATION TECHNIQUES

C-Number	Illinois Coal Member	As (ppm) ± σ AAO column	As (ppm) distillation
C-14970	No. 6	1.9 ± 0.3	2.1
C-15384	No. 5	7.5 ± 0.4	7.4
C-16264	No. 5	9.5 ± 0.4	9.6
C-16317	No. 6	24.4 ± 0.7	24
C-14796	No. 5	29 ± 5	28
C-15566	No. 2	89 ± 1	93

This method of As analysis is much faster than the distillation method and provided a check for previous As results. An excellent separation of As from Sb is obtained by this procedure.

Determination of Ga in Low-Temperature Coal Ash

Oven-dried LTA samples (100 mg) are weighed into two-fifths-dram snap-cap polyethylene vials, heat-sealed, and irradiated for 2 hours along with standard solutions prepared from pure Ga metal.

Ga (5 mg) and Zn (30 mg) carriers are added to each irradiated ash sample, which is then fused with NaOH in a nickel crucible. (A tracer study showed that no Ga is lost during fusion.) After the fusion melt is dissolved in 25 to 50 ml of water and a mixed sulfide precipitate has formed, the solution is filtered and adjusted to pH 8 with HCl, at which point Ga is coprecipitated with the $Zn(OH)_2$. The hydroxide precipitate is then filtered and dissolved in 8M HCL (15 ml), and the Ga is extracted from the resulting solution with isopropyl ether (15 ml). Gallium is then back-extracted from the organic fraction with 15 ml of water; extraction and back-extraction are repeated and the combined water extracts are counted. Some ^{76}As follows the Ga, but there is no interference with the 0.832 MeV photopeak of 14-hr ^{72}Ga. Radiochemical yields are determined by re-irradiation; they are within the 46 to 74 percent range.

The possibility that ^{72}Ga might be produced during irradiation by a (n,p) reaction with ^{72}Ge, as well as by the (n,γ) reaction with ^{71}Ga, was investigated. Two milligrams of pure Ge metal was irradiated along with samples of coal ash in a regular run and subsequently counted. No radiochemical separation is needed for the Ge metal, as there is no spectral interference between Ge and Ga. Less than 0.02 μg of "apparent" Ga was produced in Ge metal. Therefore, for every part of Ge in coal ash, the contribution to ^{72}Ga is less than 10^{-5}.

The average relative standard deviation of the technique is about 8 percent for replicate samples.

Determination of Zn and Cd in Low-Temperature Coal Ash

Oven-dried LTA samples (100 mg) are weighed into two-fifths-dram snap-cap polyethylene vials, heat-sealed, and irradiated for 2 hours along with standard solutions prepared from pure Zn metal and pure Cd metal.

Ten mg of Zn and 4 mg of Cd carriers are added to the irradiated ash sample, and are fused with NaOH (2 g) in a nickel crucible. (A tracer study showed that no Zn or Cd is lost during fusion.) The fusion melt is dissolved in 50 ml of distilled water, and 25 ml of 8M HCl is added so that the resulting solution is 2M in HCl. The solution is then loaded onto a Dowex 1 by 8 (100 to 200 mesh) anion exchange column (6 g resin) that has been pre-equilibrated with 2M HCl (30 ml). After the column is rinsed with 2M HCl (20 ml), Zn and Cd are eluted with 60 ml of distilled water in the same fraction, and Zn is determined immediately from the intensity of the 0.438 MeV photopeak of 13.8-hr ^{69m}Zn. For Cd, a decay period of one week from the time of irradiation is required so that 13.8-hr ^{69m}Zn completely decays. The count rate of the 0.523 MeV photopeak of 54-hr ^{115}Cd is then measured. Radiochemical yields are determined by re-irradiation and are in the 80 to 95 percent range for Zn and are quantitative for Cd. The average relative standard deviation is 25 percent for Zn and better than 10 percent for Cd.

Determination of Hg in Whole Coal

From 0.6 to 1.0 g of coal (hand-ground to 20 mesh and air-dried) is accurately weighed into a two-fifths-dram polyethylene snap-cap vial. Hand grinding of coal samples to -20 mesh is recommmended to avoid excessive heating and possible loss of Hg. A 1.0 ml aliquot of a 10.3 mg per ml standard solution of Hg^{++} (as nitrate) is sealed in a similar polyethylene vial. Samples and standard are simultaneously irradiated for 2 hours; one day must be allowed for the preferential decay of shorter-lived radioisotopes (such as ^{24}Na, ^{31}Na, and ^{56}Mn).

Each sample is mixed 1-to-1 with 60-mesh Norton Alundum RR (Al_2O_3), transferred to a 4-inch porcelain boat (Fisher Combax, size A), and covered with Alundum. The boat, previously impregnated with 2 mg Hg^{++} carrier (as nitrate), is placed in a 1-inch-diameter Vycor tube and the contents then combusted slowly with a Bunsen burner (~500° to 600° C). An oxygen flow of about 50 to 75 ml per minute is maintained through the tube. The gaseous and volatilized products are bubbled through two consecutive 100 ml vacuum traps, each containing 20 ml of a 3.25 pH sodium acetate-acetic acid buffer solution (Hinkle, Leong, and Ward, 1966), 40 ml of saturated bromine water, and 30 mg of Hg^{++} (as nitrate). The combustion process requires about 1 hour to insure controlled burning and efficient transfer of gases to the traps. (CAUTION: Sample should be burned very gradually, as there is danger of violent explosion.) Approximately 250 ml of 2M HCl is used to wash the glassware and the Vycor tube and is then combined with the trap solutions. The resulting solution (~450 ml) is passed through a column 1 cm in diameter containing 3.5 ml of Dowex 2 in the chloride form. After radioactive interferences are eluted with 40 ml of water and 40 ml of 2M HCl, the resin is transferred to a 100-ml polystyrene bottle, allowed to settle uniformly, and then counted for ^{197}Hg ($t_{1/2}$ = 65 hours, 66 KeV gamma ray).

A 0.10 ml aliquot of the irradiated standard is diluted to 100 ml with 2M HNO_3. One ml of this solution is immediately pipetted into a porcelain boat (already impregnated with 2 mg of inactive Hg^{++}) and air-dried. About 1 g of unirradiated coal is mixed with Alundum, placed in the boat, covered with Alundum, and burned in the same manner as the irradiated samples.

Recovery of Hg in the process is 67 ± 15 percent. The amount of Hg in a sample is calculated by comparing the height of the photopeak of the sample to that of the standard. The average relative standard deviation of the method is 20 percent, and the detection limit is 0.01 ppm for a 1-gram sample and 2-hour irradiation.

Comparisons of Hg values determined by this method with preferred values from a U.S. Bureau of Mines round-robin study (Schlesinger and Schultz, 1972) are given in table M. The accuracy of this method is excellent.

Alternate Determination of Hg in Coal

The method of Rook, Gills, and LaFleur (1971) was modified and utilized to determine Hg during the latter stages of this investigation. The standards, sample preparation, irradiation procedure, and combustion are essentially the same as previously described for Hg.

This procedure differs in that combustion products (including Hg) are collected in a cold-trap, which is cooled by dry ice. After complete combustion of the coal sample, the cold-trap tube is warmed to room temperature and the mercury is washed out with HNO_3. A further refinement of the method consists of the removal of ^{82}Br by precipitation as AgBr (the $HgBr_2$ remains soluble). The resulting solution is decanted and counted for ^{197}Hg. The Hg standard is treated identically. Radiochemical yield determinations are obtained by re-irradiation and range from 80 to 90 percent. The average relative standard deviation is 15 percent, and the detection limit is 0.01 ppm for a 1-gram sample and 2-hour irradiation. Analyses of the standard coal NBS-1630 using this method give Hg values in excellent agreement with the standard value (0.13 ppm).

TABLE M—COMPARISON OF Hg VALUES WITH PUBLISHED DATA*

Coal location	Best value (ppm)	ISGS (ppm)
Belmont Co., Ohio	0.15 ± 0.03	0.15, 0.17
Harrison Co., Ohio	0.41 ± 0.06	0.45, 0.46
Jefferson Co., Ohio	0.24 ± 0.04	0.23, 0.30
Kanawha Co., W. Virginia	0.07 ± 0.02	0.09, 0.08
Washington Co., Pennsylvania	0.12 ± 0.04	0.13, 0.14
Clay Co., Indiana	0.07 ± 0.02	0.08, 0.11
Muhlenberg Co., Kentucky	0.19 ± 0.03	0.24, 0.23
Rosebud Co., Montana	0.061 ± 0.007	0.07, 0.06
Henry Co., Missouri	0.16 ± 0.06	0.17, 0.18, 0.19
Montrose Co., Colorado	0.05 ± 0.01	0.05, 0.05, 0.05
Navajo Co., Arizona	0.06 ± 0.01	0.05, 0.05, 0.07
NBS SRM-1630 (West Virginia)	0.13	0.14

* Schlesinger and Schultz, 1972.

Determination of Sb in Whole Coal

In a manner similar to that described in the Hg procedure, 0.6 to 1.0 g of air-dried coal is hand ground, weighed, and irradiated with a standard. The irradiated sample, ~100 mg benzoic acid, and from 10 to 30 mg of accurately weighed Sb_2O_3 carrier are placed in a Parr combustion bomb and burned at an oxygen pressure of 25 atmospheres. The contents of the bomb are rinsed into a beaker with concentrated HCl, and digested on a hot plate for 1 hour, and the mixture is filtered. The filter paper and contents are vigorously heated with 100 ml of 1M KOH and 4 ml 30 percent H_2O_2 for 2 hours and then cooled and filtered.

The filtrates are combined and diluted to ~1000 ml, and H_2S is passed through the solution. The sulfide precipitate is filtered, dissolved in 20 ml of aqua regia, and evaporated to dryness. The residue is then treated with 1 g of $NH_2OH \cdot HCl$, dissolved in 2 ml of 4M HCl, and evaporated to dryness. The residue is redissolved in 1 ml of 0.5M NH_4SCN-2M HCl (Hamaguchi et al., 1969) and loaded on a Dowex 2 column (~5 ml in SCN^- form), which is then eluted with 15 ml of 0.5M NH_4SCN-0.5M HCl (to remove As) and 10 ml of 0.005M NH_4SCN-0.5M HCl. Subsequently, the Sb fraction is eluted with 150 ml of 2N H_2SO_4, and 50 ml of concentrated HCl is added to it.

The solution is counted for ^{122}Sb ($t_{1/2}$ = 2.8 day, 0.56 MeV γ-ray). Radiochemical yields are determined by re-irradiation and range from 30 to 55 percent. The average relative standard deviation of the method is 20 percent.

Determination of Br in Whole Coal

From 0.6 to 1.0 g of coal (hand-ground to 20 mesh and air-dried) is accurately weighed into a two-fifths-dram polyethylene snap-cap vial. One ml of a standard solution containing 111 mg of Br as NH_4Br is sealed in a similar vial. Samples and standards are simultaneously irradiated for 2 hours, and about 1 day is allowed for the decay of shorter-lived radioisotopes.

Each sample is mixed 1 to 1 with 60-mesh Norton Alundum RR (Al_2O_3) and transferred to a 4-inch porcelain boat. Twenty mg Br as NH_4Br solution is added to the boat and allowed to dry. The contents of the boat are then covered with Alundum and the boat is placed in a 1-inch Vycor tube. Combustion of the sample takes place slowly using a Bunsen burner (~500° to 600° C) in an oxygen-flow system, with a flow rate of between 50 and 75 ml per minute. The gaseous and volatilized products are bubbled through two consecutive traps containing 3M NaOH or KOH. The first trap contains 200 ml and the second 80 ml. (CAUTION: Sample should be burned very gradually, as there is danger of violent explosion.)

After combustion, all glassware is washed with water, and the wash liquid is combined with the alkali trap solutions. The combined solutions are then counted for ^{82}Br ($t_{1/2}$ = 36 hours, 0.56 MeV γ-ray).

A 5-ml aliquot is re-irradiated for chemical yield determination, which varies from 49 to 77 percent. The average relative standard deviation is 10 percent.

Instrumental Neutron Activation Analysis of Mn in Whole Coal

From 0.6 to 1.0 g of the coal (hand-ground and air-dried) is accurately weighed into a two-fifths-dram polyethylene snap-cap vial. One ml of a solution containing a known quantity of Mn^{++} (from 100 to 200 μg) is heat-sealed into a similar vial. Samples and standard are simultaneously irradiated for only 15 minutes in a thermal neutron flux of about 0.7×10^{12} neutrons cm^{-2} sec^{-1}.

After approximately 2 hours are allowed for the preferential decay of the shorter-lived radioisotopes (e.g., ^{31}Si and ^{38}Cl), the samples are transferred to unirradiated containers, counted, and compared with the standard for ^{56}Mn ($t_{1/2}$ = 2.6 hours, 0.84 MeV γ-ray).

The average relative standard deviation of this instrumental technique is 4 percent.

Instrumental Neutron Activation Analysis of Na in Whole Coal

From 0.6 to 1.0 g of coal (hand-ground and air-dried) is accurately weighed into a two-fifths-dram polyethylene snap-cap vial. A 1.0-ml solution containing a known amount of Na^+ (1000 μg) is heat-sealed in a similar vial. Samples and standard are simultaneously irradiated for only 10 minutes in a thermal neutron flux of about 0.7×10^{12} neutrons cm^{-2} sec^{-1}.

After allowing overnight for the preferential decay of the shorter-lived radioisotopes, the samples are counted for ^{24}Na ($t_{1/2}$ = 15.4 hours, 1.37 MeV γ-ray) and compared with the standard. Corrections are made for the average blank contributions of Na from the vials.

The average relative standard deviation of this instrumental technique is 5 percent.

Ion-Selective Electrode Method for Determination of F in Whole Coal

A 1-gram coal sample, ground to pass a 100-mesh screen, is mixed with about 0.25 g benzoic acid (primary standard) and placed in a fused quartz sample holder within a Parr combustion bomb that contains 5 ml of 1N NaOH. The bomb is then pressurized to about 28 atmospheres with oxygen and fired. At least 15 minutes must elapse before the bomb is depressurized. The bomb contents are then rinsed with three 5-ml aliquots of distilled water into a 50-ml plastic beaker (plastic-ware is used for all subsequent operations in this method).

The beaker contents are magnetically stirred with a Teflon bar while the pH is adjusted to 5.2 to 5.5 with 0.5N H_2SO_4. (The initial pH before adjustment is about 7.0.) The beaker is then placed in a hot water bath for about 10 minutes and removed, and the contents are again stirred to drive off most of the dissolved CO_2. Five ml of 1M sodium citrate-citric acid buffer (pH 6.3) containing 0.2M KNO_3 is added to the beaker contents. The total volume is adjusted to 50 ml with distilled water and cooled to room temperature. At this time, the potential is read. In some cases, about 10 minutes is required for equilibrium to be reached. The F concentration is calculated by the known addition method (1 ml of 0.01M F is added and the potential of the solution read again).

The pH is critical for the initial potential reading; at 5.0 to 5.5, final results tend to be low because of F^- complexing with H^+. Above pH 7.0, results are high because of interference from OH^- or HCO_3^- at concentrations of 1000 times that of the F.

An independent fusion method for sample preparation was used to determine whether F is lost during combustion of coal samples in a pressurized bomb. The procedure for the alternate fusion method is as follows: 3 grams of coal is mixed with 5 grams anhydrous Na_2CO_3 and the mixture is placed into a platinum crucible. Approximately 2 grams more of the Na_2CO_3 are used to cover the mixture. The crucible and contents are then heated in a furnace at about 475° C for 24 hours, followed by final heating over an air-boosted Meker burner (about 1000° C) for 15 minutes to fuse the mixture. After cooling, the crucible contents are extracted with hot water and the pH is reduced to 5.2 to 5.5 with 1N H_2SO_4. The solution is warmed in hot water to assist in the removal of CO_2, and about 25 ml of 1M sodium citrate-citric acid buffer (pH 6.2) is added to buffer the solution and to release any fluoride which may have been complexed by iron, etc., at the lower pH. The solution is made to a known volume (generally 250 ml), and an aliquot is taken for reading the potential with the fluoride ion-selective electrode. A known addition of standard fluoride solution is made and the potential is read again. From these readings the fluoride concentration is determined.

As determined by the fusion method, the fluoride content of NBS standard coal sample 1630 is 86 ppm. The average value for five replicate determinations made by the bomb combustion method on 1-g coal samples is 80 ± 4 ppm. Using the bomb combustion method, the results of duplicate determinations for coal sample C-14796 are 113 and 111 ppm F; a single value obtained by the fusion method is 122 ppm. In addition to these comparative results, we found that F values determined by the alternate fusion procedure are in good agreement with those determined by a calorimetric-fluoride distillation method. These comparisons were made on samples of gypsum containing about 1 percent F. Thus, it is reasonable to conclude that F is not being lost during sample preparation by either procedure, and that the bomb-combustion ion-selective electrode procedure, which gives reproducible results for F in coal, also provides an accurate appraisal of the F present.

TRACE ELEMENT DETECTION LIMITS FOR ALL METHODS

Table N gives trace element detection limits for each method used. Whole coal detection limits are given for those methods used in the direct analysis of raw coal. However, it is not possible to give whole coal detection limits for those methods which require a coal ash for the analysis sample, because the ash content of the coals directly affects the detection limit, as calculated to the whole coal. For those methods, detection limits are given on the ash basis.

U.S. EPA-NBS TRACE ELEMENT SYMPOSIUM

A large-scale interlaboratory comparison of trace element results for coal, fly ash, fuel oil, and gasoline was completed by the U.S. Environmental Protection Agency and the National Bureau of Standards. Our results for the coal and fly ash were among those submitted by many laboratories. During the recent Trace Element Symposium held in Research Triangle Park, North Carolina, results from all laboratories were distributed to those persons in attendance. Table O compares the trace element values obtained for the coal by the methods previously described with those obtained by the National Bureau of Standards, and with the mean values of the trace element concentrations from all other participating laboratories. Our results for F, As, Be, Cd, Cr, Hg, Mn, Ni, Pb, and Se in the interlaboratory coal sample agreed exceptionally well with the NBS certified* values.

During the symposium, the need for reliable methods and for analytical chemists experienced in trace element methodology was repeatedly emphasized. In particular, the lack of agreement of cadmium results for coal was cited; none of the methods used by the participating laboratories could be classified as suitable. Further, little or no data were reported for the trace elements F, Co, Sn, Ge, Ga, Sb, Mo, B, Br, Tl, or Bi.

PREFERRED ANALYTICAL PROCEDURES

Table P summarizes the method or combination of methods used for determining our recommended or best values for whole coal reported in table 1. For most elements, results from two or more methods were available. As previously discussed, extensive inter- and intra-laboratory check analyses were made, and the ultimate choice of the best technique(s) was made on the basis of consistent achievement of accuracy and precision. Where more than one method is listed in table P, results from these were averaged.

Similarly, table Q indicates the choice of analytical method for the recommended values reported for the float-sink samples (table 10). Because data had to be consistent within a series of specific-gravity fractions for washability calculations, only one analytical method was used instead of a multiple approach and averaging.

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* Although still subject to change, especially in the cases of Ni and Mn, these certified values will probably be the values given when this coal sample is offered by NBS as a standard reference material.

TABLE N—SUMMARY OF DETECTION LIMITS FOR METHODS USED IN THIS INVESTIGATION

	ppm in coal ash				ppm in whole coal	
Element	Atomic absorption	Neutron activation	Optical emission-photographic	Optical emission-spectrometric	Neutron activation	X-ray fluorescence
Ag			4.0			
Al						300
As		1.2				2
B			25	2		
Be			1	1		
Br					1	1.5
Ca						12
Cd	2.5	50				
Cl						36
Co			20	3		
Cr			45	1.5		
Cu	20		4	1.5		
F	Detection limit for F by ion-selective electrode = 10 ppm in whole coal.					
Fe						36
Ga		1				
Ge			40	1.5		
Hg					0.01	
K						9
Mg						25
Mn					2	
Mo			25	3		
Na					0.5	
Ni	20		7	1		3.5
P						20
Pb	20		30	5		2.5
S						72
Sb					0.1	
Sn				3		
Se		1.8				
Si						240
Ti						27
V			45	5		0.5
Sn	20		80			4
Zr			5			

TABLE O—COMPARATIVE RESULTS FOR EPA-NBS INTERLABORATORY TRACE ELEMENT STUDY

	Parts per million in moisture-free coal							
			Illinois State Geological Survey*					
				Atomic absorption				
Element	NBS 1632 probable certified values	All labs grand mean	Neutron activation	LTA	HTA	Optical emission	X-ray fluor.	Ion elec.
As	5.9 ± 0.6	6.24	5.7					
Cd	0.19 ± 0.03	0.9**		< 0.4	< 0.4			
Cr	20.2 ± 0.5	22.7		24	22	22		
Cu	18 ± 2			18	23	28	22	
Hg	0.12 ± 0.02	0.22	0.18					
Mn	40 ± 3	41.3	39					
Ni	15 ± 1	19.0		16	16	26	22	
Pb	30 ± 9	30.4		22	32	24	26	
Se	2.9 ± 0.3	4.6	2.8					
Tl	0.59 ± 0.3							
Th	(3)							
U	1.4 ± 0.1	1.7						
V	35 ± 3	34.9				54		
Zn	37 ± 4	29.5**		40	38		49	
Fe	8700 ± 300						1.12	
Be	(1.5)	1.75				1.72		
F		83.5**						80.4
S		1.28%					1.26	

( ) - Information value only.
* - Average of at least four or more determinations.
** - Questionable mean; wide scatter or limited data.

TABLE P—ANALYTICAL PROCEDURES USED TO DETERMINE RECOMMENDED TRACE ELEMENT VALUES

Element	Procedure
Hg, Sb, Se, As, Ga, Mn, Na	NAA
Fe, Ti, Al, Si, K, Ca, S, Cl, Mg, Br, P	X-RF
Be, Ge, Co, Cr	OE-DR, OE-P
Cd, Zn	AA
Pb, Cu	AA, OE-DR
Ni	OE-DR, AA, OE-P, X-RF
F	ISE
Zr	OE-P
V	OE-DR, OE-P, X-RF
Mo, Sn, B	OE-DR

TABLE Q—ANALYTICAL PROCEDURES USED FOR RECOMMENDED VALUES FOR FLOAT-SINK SAMPLES

Element	Procedure
Hg, Sb, Se, As, Ga, Mn, Na	NAA
Fe, Ti, Al, Si, K, Ca, S, Cl, Mg, Br, P	X-RF
Cd, Zn, Pb, Cu, Ni	AA
Be, Ge, Co, Cr, V, Mo, B	OE-DR
Zr	OE-P

SUMMARY OF ANALYTICAL METHODS USED FOR THE DETERMINATION OF TRACE ELEMENTS*

Antimony (Sb)

To better establish the accuracy of the neutron activation radiochemical procedure developed for whole coal, a sample was analyzed for Sb by an independent instrumental neutron activation method. Results obtained by the two methods are in good agreement. Results for Sb determined in low-temperature coal ash by yet another radiochemical procedure also compared favorably with those obtained by the whole coal radiochemical separation method described herein.

Volatilization studies show that significant amounts of Sb were lost from one coal during low-temperature ashing. The radiochemical method for whole coal eliminates the possibility of unpredictable Sb losses.

Arsenic (As)

Two methods, neutron activation analysis of LTA and X-ray fluorescence analysis of whole coal, are used for the determination of As. Neutron activation results, calculated to the whole coal basis, compare well with X-ray fluorescence values at the higher concentrations. However, the latter method frequently exhibits a high bias for low As concentrations. The recommended values for As given in table 1 are those determined by the neutron activation method.

Beryllium (Be)

Direct reading and photographic optical emission methods give comparable results for Be in high-temperature coal ash. The recommended whole coal values in table 1 are an average of results from both methods.

Bromine (Br)

The neutron activation and X-ray fluorescence results obtained for Br in whole coal have been shown to be in good agreement. However, the X-ray fluorescence procedure is much more rapid and has good precision. The Br results reported in table 1 were determined by this procedure.

Cadmium (Cd)

Cadmium determinations of low-temperature coal ash samples made by using atomic absorption and neutron activation methods are in good agreement. Determinations by the University of Illinois Environmental Analytical Laboratory performed by an anodic-stripping voltammetry procedure agree very well with atomic absorption determinations of Cd in coal ash. Our recommended values, calculated to the whole coal basis, are those determined by atomic absorption.

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* In this summary, frequent reference is made to comparison of results obtained by two or more analytical methods. Because of the huge number of analyses involved, these data were not included in table 1, which records only recommended values. However, all comparisons for 25 coals were reported in Ruch, Gluskoter, and Shimp (1973).

Chromium (Cr)

Recommended values for Cr, calculated to the whole coal basis, are the means of results from direct reading and photographic optical emission methods. Atomic absorption results for Cr also agree well with those obtained by these two methods.

Cobalt (Co)

Good agreement for cobalt concentrations determined in coal ash by three analytical methods—photographic and direct-reading optical emission and neutron activation—was obtained, although photographic optical emission values tend to be higher for samples having low concentrations. Recommended values in table 1 are the mean concentrations, expressed on the whole coal basis, as determined by the photographic and direct-reading optical emission methods.

Copper (Cu)

X-ray fluorescence, atomic absorption, and direct-reading and photographic optical emission results compare well for Cu in whole coal, although X-ray fluorescence values tend to be higher and those for photographic optical emission lower. The Cu values reported in table 1 are the means of atomic absorption results from the analyses of low-temperature ash and direct-reading optical emission results from the analyses of high-temperature ash.

Fluorine (F)

Fluorine determinations were performed by a commercial laboratory and by the Illinois State Geological Survey. The F results of the commercial laboratory's distillation-colorimetric method are generally higher than those determined in our laboratories using the ion-selective electrode procedure. Extensive checking of our results with those of other laboratories and the use of independent methods of analysis show that results obtained by the ion-selective electrode technique are more accurate. Thus, the recommended values given in table 1 were determined by the ion-selective electrode method.

Gallium (Ga)

Results obtained for Ga by the radiochemical procedure developed for low-temperature coal ash agree with data given by Zubovic, Stadnichenko, and Sheffey (1964). Our average for Illinois coal is 3.6 ppm, and their average value is 4.1 ppm. The literature values for U.S. Geological Survey standard rock W-1 range from 16 to 20 ppm (Fleisher, 1969); our value is 21 ppm.

Germanium (Ge)

Photographic and direct-reading optical emission results for Ge in high-temperature coal ash are in good agreement. The recommended values in table 1 are the mean values of whole coal concentrations determined by both methods.

Lead (Pb)

X-ray fluorescence, atomic absorption, and photographic and direct-reading optical emission results for Pb are in good agreement, although the direct X-ray fluorescence analysis of whole coal tends to give higher results than the other methods, which require coal ash for analysis. The recommended values in table 1 are means of atomic absorption and direct-reading optical emission spectrometric results.

Mercury (Hg)

Mercury results from the radiochemical procedure previously developed (Ruch, Gluskoter, and Kennedy, 1971) are in good agreement with those reported in the 1971 U.S. Bureau of Mines round-robin study (table M). The values obtained by this method are being reported without further independent checks. The NBS method (Rook, Gills, and LaFleur, 1971) is used interchangeably.

Nickel (Ni)

Determinations of Ni by X-ray fluorescence, atomic absorption, and direct-reading and photgraphic optical emission methods have shown that all results are in good agreement when the values are calculated to the whole coal basis. The recommended values in table 1 are means of results from all of these methods.

Selenium (Se)

The neutron activation radiochemical separation technique for low-temperature coal ash yields precise values on replicate samples. When calculated to the whole coal basis, our value of 2.0 ppm Se compares very well with the provisional value for NBS-SRM-1630 coal standard (Se = 2.1 ppm). Comparison of our results with those of the previously mentioned National Bureau of Standards-U.S. Environmental Protection Agency round-robin indicate that this method is accurate for the analysis of coal.

Vanadium (V)

Vanadium determinations made by X-ray fluorescence analysis of whole coal and by both direct-reading and photographic optical emission analyses of high-temperature ash sometimes exhibit a wide scatter. Our recommended values, expressed as concentrations in whole coal, are the means of selected values determined by all three methods, with very high or low individual results being deleted.

Zinc (Zn)

X-ray fluorescence, atomic absorption, and photographic optical emission methods of analyses all yield acceptable results for Zn when values are given on the whole coal basis. Photographic optical emission values tend to be slightly lower than those of other methods. As previously mentioned, inconsistent results for high levels of Zn are associated with localized mineralization and sample inhomogeneity (see also the discussion of the scanning electron microscope). Finer grinding (-325 mesh) of coal samples should improve the analytical precision for very high concentrations of Zn. The recommended values in table 1 are those determined by atomic absorption.

Phosphorus (P), Boron (B), Zirconium (Zr), Molybdenum (Mo), and Tin (Sn)

Each of these elements has been determined by a single method only, without further confirmation of the values. Phosphorus was determined by X-ray fluorescence analysis of whole coal; B, Zr, Mo, and Sn were determined in coal ash by optical emission spectroscopy. The Mo values are suspected of being biased low.

SUMMARY OF ANALYTICAL METHODS USED FOR THE DETERMINATION OF MAJOR AND MINOR CONSTITUENTS

The results in tables 2, 3, and 4 give X-ray fluorescence values (percent of moisture-free whole coal) for Si, Ti, Al, Fe, Ca, K, Mg, S, and Cl; neutron activation values for Na; and gravimetric values for the percentage of low- and high-temperature ashes in coal. Concentrations of each element have been determined in both whole coal samples and samples of low- and high-temperature ash prepared from splits of the coal sample, and good agreement among results has been obtained for the three different coal sample preparation techniques when all values are expressed as concentrations in whole coal. The reported values given in table 1 for these constituents were all obtained from direct analysis of whole coal. In addition, the X-ray fluorescence results for S and Cl agree well with the corresponding values obtained by wet-chemical (ASTM) methods.

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